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Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis—A review

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ABSTRACT

Biomass gasification is an interesting technology in the future development of a worldwide sustainable energy system, which can help to decrease our current dependence on fossil fuels. Biomass gasification is a thermal process where solid fuel is converted into a useful gas using several gasifying agents such as air, and steam. The producer gas has a great number of applications. The most important is being combustion for power and heat generation as well as raw gas for production of fuels or chemicals. This review mainly presents the recent progresses on tar elimination during the biomass gasification. Then, novel non-catalytic absorption and adsorption methods of tar removal under ambient temperature conducted by our laboratory members were also explained. In our opinion, the tar removal can be conducted by combination of catalytic reforming in the gasifier and oil materials adsorption in the scrubber. Furthermore, the tar catalytic reforming is a most significant step during biomass gasification or pyrolysis. Thus, the development of reasonable catalysts for tar elimination has been faced with a significant challenge in current society.

Contents

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1. Introduction

The contribution of biomass to the world's energy supply is presently estimated to be around 10% to 14% [1]. Biomass gasification is an interesting technology in the future development of a worldwide sustainable energy system, which can help to decrease our current dependence on fossil fuels. Biomass gasification is a thermal process where solid fuel is converted into a useful gas using several gasifying agents such as air, and steam. The producer gas has a great number of applications. The most important is being combustion for power and heat generation as well as raw gas for production of fuels or chemicals [2]. However, gasification of biomass produces not only useful fuel gases but also some unwanted byproducts. Among them, tar is recognized as one of the most problematic parameters in any gasification system [3,4]. These tars can cause several problems, such as cracking in the pores of filters, forming coke and plugging them, and condensing in the cold spots and plugging them, resulting in serious operational interruptions [5]. Moreover, these tars are dangerous because of their carcinogenic character, and they contain significant amounts of energy that can be transferred to the fuel gas as H_2, CO, CH_4, etc. In addition, high concentrations of tars can damage or lead to unacceptable levels of maintenance for engines and turbines. Tars are defined as a generic (unspecific) term comprising all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1–C6) and benzene [6]. Fig. 1 shows the typical composition of biomass tars [7]. However, this composition depends on the type of fuel and the gasification process.

In general, tars can be removed by physical, noncatalytic (e.g., thermal cracking), and catalytic tar elimination processes [8]. Various mechanical/physical gas cleanup systems exist for removal of both particulates and tar from gases produced by biomass gasification. Often these overlap, particularly when tar is present as liquid droplets. Based on application, mechanical/physical methods are divided into two categories: dry and wet gas cleaning. Dry gas cleaning is usually used prior to gas cooling where the temperature is greater than 500 °C and partly below 200 °C after gas cooling, while wet gas cleaning is used after the gas cooling and typically about 20–60 °C [9]. A summary of particles and tar reduction from producer gas in various mechanical/physical methods are as shown in Table 1 [10]. Physical methods involve filters and scrubbers, where the tar is separated in a condensed form. However, a great disadvantage of this strategy is that the crude synthesis gas needs to be cooled down before the final separation. Furthermore a huge amount of waste water is produced. In addition to that tar can be removed thermally. Thereby temperature from over 1000 °C is required to remove the undesired components completely [11].

From an economic and technical point of view the catalytic process therefore is a promising alternative. Great advantage of this strategy is that a high degree of purity can be achieved at low temperature and simultaneous increase of the fuel value [11]. Depending on the experimental conditions, catalytic methods can be classified into reforming, cracking, hydrogenation and selective oxidation. To meet the demands of an energy efficient process, a tar removal strategy in the temperature range from 350 °C to 700 °C is desirable. From both the outlet temperature of the gasification process (900–1300 °C) and the operating temperature of the following steps, like Fischer-Tropsch (300–400 °C), in a way that the strategies for tar removal strategies, this temperature-range results are highly restricted. A tar removal strategy without the already mentioned problems which fulfills the requirements is the catalytic partial oxidation. The addition of a small amount of oxygen (stoichiometric towards tar) causes an efficient tar reduction to a fuel gas based on CO/H_2. A special challenge is indeed the choice of the catalyst, since the tar needs to be removed without oxidizing the synthesis gas components. The general catalytic tar removal strategy is shown in Fig. 2 [11].

Catalytic tar conversion is a technically and economically interesting approach for gas cleaning. Such an approach is

Table 1
Reduction of particles and tar in various producer gas cleaning systems (with various definitions of "tar") [10].

	Temperature (°C)	Particle reduction (%)	Tar reduction (%)
Sand bed filter	10–20	70–99	50–97
Wash tower	50–60	60–98	10–25
Venturiscrubber			50–90
Rotationla atomizer	< 100	95–99	
Wet electrostatic precipitator	40–50	> 99	0–60
Fabric filter	130	70–95	0–50
Rotational particle separator	130	85–90	30–70
Fixed bed tar adsorber	80		50
Catalytic tar cracker	900		> 95

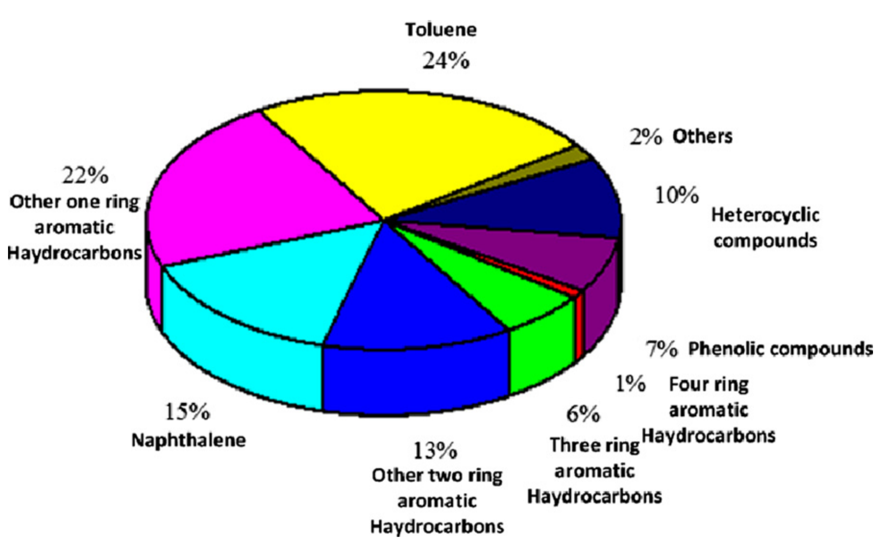


Fig. 1. Typical composition of biomass tars (modified) [7].

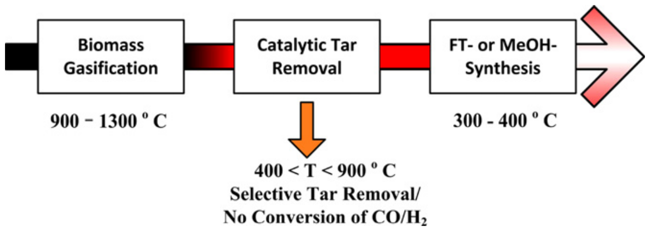


Fig. 2. Catalytic tar removal strategy [11].

intuitively interesting because it has the potential to increase conversion efficiencies while simultaneously eliminating the need for the collection and disposal of tars. The catalytic conversion of tars is commonly known as hot gas cleaning. The research on catalytic tar conversion involves two methods [12,13]: One approach involves incorporating or mixing catalyst with the feed biomass to achieve so called catalytic gasification or pyrolysis (also called in situ). This method is a one of the primary methods used for tar reduction, where the tar is removed in the gasifier itself. In the second approach, the gasifier producer gas is treated downstream of the gasifier in a secondary reactor. This method is a one of the secondary methods used for tar reduction, where the tar is removed outside the gasifier. Among hot gas conditioning systems, catalytic cracking and steam reforming of high molecular weight hydrocarbons offer several advantages, such as thermal integration and high tar conversion. A large number of investigations deal with biomass gasification in fluidized bed reactors utilizing nickel based catalysts, dolomite or olivine.

This article presents, in detail, the recent works on the catalytic tar elimination after biomass gasification. Widely used catalysts like Ni-based catalysts, olivine, dolomite etc. are introduced, and novel developed like nano-Ni-based catalysts, ceramic catalysts are also recommended here. Then, novel non-catalytic absorption and adsorption methods of tar removal under ambient temperature conducted by our laboratory members were briefly explained as well.

2. Catalytic tar elimination

Tar elimination reactions are known to be kinetically limited. Therefore, the reaction rates can be increased by increasing the temperature and/or using a catalyst. However, catalysts can only increase the rate of a reaction that is thermodynamically feasible. The chemistry involved in catalytic tar decomposition of producer gas is a complex mix of hydrocarbon decomposition and equilibrium reactions. The tar reaction mechanisms have been investigated, for example, by Simell et al. [14], by using toluene as a tar component in hot catalytic gas cleanup. Based on these toluene experiments, they proposed a set of decomposition and equilibrium reactions (1), (6) and (8) summarized in Table 2. The proposed reaction scheme is complemented by reaction (7). In Table 2, toluene is replaced by C_nH_m, which is a general representation of the tar molecules in the producer gas from a biomass gasifier. In comparison to toluene, the tar composition in a gasifier includes at least 150 different tar molecules, which vary in molecular weights from that of benzene to weights higher than pyrene. As the molecular weight of the tars is increased so is usually also the dew point temperature, which normally increases the operating problems. In addition to the partial oxidation of the tar components, reaction (1) , studies have shown that steam and dry reforming reactions (1) and (6) are catalyzed by metals from group VIII [14,15]. This implies that the Fe content of the ilmenite, together with the water and carbon dioxide content in the producer gas, will induce both steam and dry reforming.

Table 2
Important decomposition and equilibrium reactions of tar removal.

Reaction	Equation	Reaction number
Potential tar decomposing reactions		
steam reforming	$C_nH_m{}^a + nH_2O \rightarrow nCO + (n+0.5m)\ H_2$	(1)
Steam dealkylation	$C_nH_m + xH_2O \rightarrow C_xH_y + qCO + pH_2$	(2)
Thermal cracking[b]	$C_nH_m \rightarrow C^* + C_xH_y + gas$	(3)
Hydro cracking	$C_nH_m + (2n-(m/2))\ H_2 \rightarrow nCH_4$	(4)
Hydro dealkylation	$C_nH_m + xH_2 \rightarrow C_xH_y + qCH_4$	(5)
Dry reforming	$C_nH_m + nCO_2 \rightarrow 2nCO + 0.5mH_2$	(6)
Cracking	$C_nH_{2n+2} \rightarrow C_{n-1}H_{2(n-1)} + CH_4$	(7)
Carbon formation	$C_nH_{2n+2} \rightarrow nC + (n+1)H_2$	(8)
Equilibrium reactions		
Water–gas shift	$CO + H_2O \rightarrow H_2 + CO_2$	(9)
Methanation 1	$CO + 3H_2 \rightarrow CH_4 + H_2O$	(10)
Methanation 2	$2H_2 + C \rightarrow CH_4$	(11)
Water gas	$CO + H_2 \rightarrow H_2O + C$	(12)
	$CO_2 + 2H_2 \rightarrow 2H_2O + C$	(13)
Boudouard	$C + CO_2 \rightarrow 2CO$	(14)

[a] C_nH_m hydrocarbons present tars.
[b] Modified.

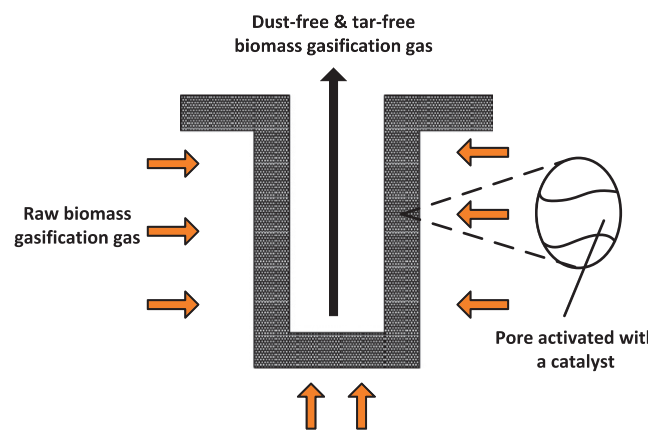


Fig. 3. Schematic representation of a catalytic candle filter.

Calculations performed by Simell et al. [14] showed that dry reforming was more thermodynamically favored than steam reforming reactions at temperatures above 830 °C. Three exothermic carbon forming reactions that are favored below 650 °C are listed in Table 2; the Boudouard reaction (14) and two water gas reactions (12) and (13). Reaction (8), listed in Table 1, is an additional carbon forming reaction which is enhanced at higher temperatures. Furthermore, the water–gas shift reaction (9) is reported to be catalyzed by Fe-based catalysts [16].

The recently developed gas cleaning technique is catalytic filter. The schematic diagram of a catalytic filter was shown in Fig. 3. This method combines the filtration for particles removal and catalytic cracking of tar from producer gas in one step. A great amount of experimental results demonstrated that the method is also considerably efficient in removing tar and particles [17–20]. It was reported that above 850 °C, a high performance for converting benzene and naphthalene was found using gas velocities typically encountered in candle filtration. The ceramic candle filter contains a nickel-based tar cracking catalyst in the support body [17]. Schematic representation and operation of the catalytic candle filter is shown in Fig. 3. Engelen et al. [19] also revealed that tar removal efficiency between 96% and 98% for naphthalene and 41% and 79% for benzene can be achieved with a co-precipitated catalytic filter disc at a filtration gas velocity of 2.5 cm/s, with 100 ppm of H_2S at a temperature of 900 °C. In the experiments of Ma et al. [21], the conversion of naphthalene

is almost complete and a 1000-fold reduction in tar content is obtained with 2.5 wt% Al_2O_3, 1.0 wt% Ni and 0.5 wt% MgO porous alumina filter discs at a typical face velocity of 2.5 cm/s, in the presence of H_2S at 900 °C. The similar result was also obtained with a mixed oxide deposit of 1.20 wt% ZrO_2+1.28 wt% Al_2O_3 followed by 0.46 wt% MgO+0.996 wt% Ni [22].

2.1. Ni based catalysts

2.1.1. Common Ni catalysts (unitary or binary)

Ni-based catalysts are extensively applied in the petrochemical industry for naphtha and methane reforming [23–39]. Meanwhile, a wide variety of Ni-based catalysts are commercially available. Especially, some studies showed that nickel based catalysts had the ability of reversing ammonia reaction, thus it is possible to reduce NO_x emission during biomass gasification [23–25].

Zhang [30] investigated tar catalytic destruction in a tar conversion system consisting of a guard bed and catalytic reactor. Three Ni-based catalysts (ICI46-1, Z409 and RZ409) were proven to be effective in eliminating heavy tars (> 99% destruction efficiency). Hydrogen yield was also improved by 6–11 vol% (dry basis). The experimental results also demonstrated that space velocity had little effect on gas compositions, while increasing temperature boosted hydrogen yield and reduced light hydrocarbons (CH_4 and C_2H_4) formation, which suggested that tar decomposition was controlled by chemical kinetics.

Coll [34] studied the model compounds like benzene, toluene, naphthalene, anthracene, and pyrene were cracked using two commercial nickel catalysts: UCG90-C and ICI46-1 at 700–800 °C. The order of these model tars reactivity was: benzene > toluene > anthracene > pyrene > naphthalene. Toluene conversion rate ranged from 40% to 80% with the ICI46-1 catalyst, and 20% to 60% for the UCI G90-C catalyst, respectively.

Simell and co-workers [39–42] reported the use of alumina and other catalysts with variable Ni content reformed toluene in various gas atmospheres at 900 °C and 0.5–20 MPa. The effects of sulfur poisoning on the activity of these catalysts for tar and ammonia decomposition had also been evaluated.

Nickel supported on silica was active for tar catalyst cracking at relatively low temperature (823 K) was described by Zhang [43]. However, these catalysts only maintained their activities for a short time because of accumulating large amounts of carbon on their surfaces. Aznar [44] and Baker [45] also mentioned the phenomena in their experiments. In order to overcome the shortcoming of the commercial Ni-based catalyst, many Ni-based catalysts were developed.

The result of Marino [46] indicated that the addition of Ni into Cu/Ni/γ-Al_2O_3 catalyst was favorable to gases yield increase and acetic acid production reduction during ethanol gasification. Magnesium, lanthanum, and titanium oxide-doped Ni–Cr/Al_2O_3 catalysts were prepared by Denis [47], and experiments were performed to assess the performance of these catalysts in steam reforming naphthalene. The experimental results revealed that the improved catalyst could promote conversion efficiency of naphthalene. After the structure analysis, it was found that MgO had a significant effect on the robustness of catalyst due to the formation of $MgAl_2O_4$ spinel phase.

Courson et al. [48–50] also developed a new Ni based catalyst by impregnating nickel oxide on olivine and calcination at 900 °C, 1100 °C and 1400 °C. X-ray diffraction, scanning electron microscopy and transmission electron microscopy coupled to energy dispersive X-ray spectroscopy analysis showed that there were interactions between the precursor and the support, which was consistent with the conclusion of Denis. After the characteristic studies, the catalyst performance tests indicated that the catalyst containing 2.8 wt% Ni calcined at 1100 °C was the optimum catalyst. Furthermore, no sintering and very little carbon deposition were observed on this catalytic surface.

Chen [51] investigated CO_2 reforming methane over NiO/γ-Al_2O_3 catalyst in a fixed/fluidized bed. Francisco [52] also compared the Ni catalyst supported on α-Al_2O_3, ZrO_2 and α-Al_2O_3–ZrO_2, and found Ni/α-Al_2O_3–ZrO_2 catalyst showed better performance. In the literature of Engelen [53], he mentioned that the 1 wt%/0.5 wt% nickel/calcium catalyst co-precipitated inside porous filter discs can effectively remove tar (> 98%) even in the presence of 100 ppm H_2S.

Recently, some researchers have tried the additive modification methods to improve the supported nickel catalysts property to achieve optimizing utilization. As the aforementioned, Ni is more suitable than Co in the steam reforming of hydrocarbons [54–59]. On the other hand, supported Co catalysts have recently been utilized for the steam reforming of oxygenates such as ethanol [60], and methanol [61], and it has been reported that Co is more effective to the steam reforming of oxygenates than Ni [62–65]. Therefore, in order to obtain high performance in the steam reforming of tar, catalysts should have high activity for both hydrocarbons and oxygenates. Development of supported metal catalysts for the steam reforming of tar derived from biomass pyrolysis has been carried out mainly by the modification of catalytically active element with co-catalysts, such as modification of Ni with CeO_2 [66–70], MnO_x [71], and Fe [72] and modification of Rh with CeO_2 [73–76]. Wang et al. [77] got research on the synergistic effect of the combination of two active elements, Ni and Co. The results presented that in the steam reforming of toluene, Co/Al_2O_3 showed higher activity and higher resistance to coke deposition than Ni/Al_2O_3, and the performance of Ni–Co/Al_2O_3 was located between that of Co/Al_2O_3 and Ni/Al_2O_3. Catalyst characterization indicates the formation of the well-mixed Ni–Co solid solution alloy. High performance of the optimized Ni–Co/Al_2O_3 catalyst in the steam reforming of tar is suggested to be due to the synergy between Ni and Co atoms on the Ni–Co alloy surface in the steam reforming of oxygenates.

2.1.2. Palygorskite-supported Fe and Ni catalyst

Recently iron-based catalyst and additive Fe attracted more attention of researchers [78]. Liu studied the different additives (Fe, Mg, Mn, Ce) on catalytic cracking of biomass tar over Ni_6/palygorskite [79–81]. Liu [79] found that the effect of additives (Fe, Mg, Mn, and Ce) on a 6%Ni/PG catalyst was different. Among the additives, the effect of Fe on the 6%Ni/PG catalyst was strong compared with that of Mg, Mn, and Ce. Tar conversion and H_2 yield were 98.2% and 56.2%, respectively, when the Fe loading was increased to 8%. Fe–Ni alloy and Fe–Ni spinel were found on the 6%Ni/PG catalyst modified by Fe, which enhanced the catalyst activity for breaking C–C and C–H bonds, increased carbon deposition and H_2 yield, and showed the synergistic effect of the active components of Fe and Ni.

Liu [80] also investigated catalytic cracking of tar derived from rice hull gasification over palygorskite-supported Fe and Ni. Comparing the carbon deposits as shown in Fig. 4, it is observed that carbon deposition on Fe_x–Ni_6/PG catalysts was higher than Fe_6–Ni_y/PG catalysts on the whole. Moreover, the two figures also showed the effect of Ni and Fe loading on the hydrogen yield derived from catalytic cracking biomass tar. It is seen that high concentration of iron can improve the conversion of carbon and high concentration nickel was more favorable for the increase in yield of hydrogen. Obviously, it indicates that the addition of Ni played a more important role in decreasing carbon deposit compared with Fe. As well known, carbon deposit would decrease

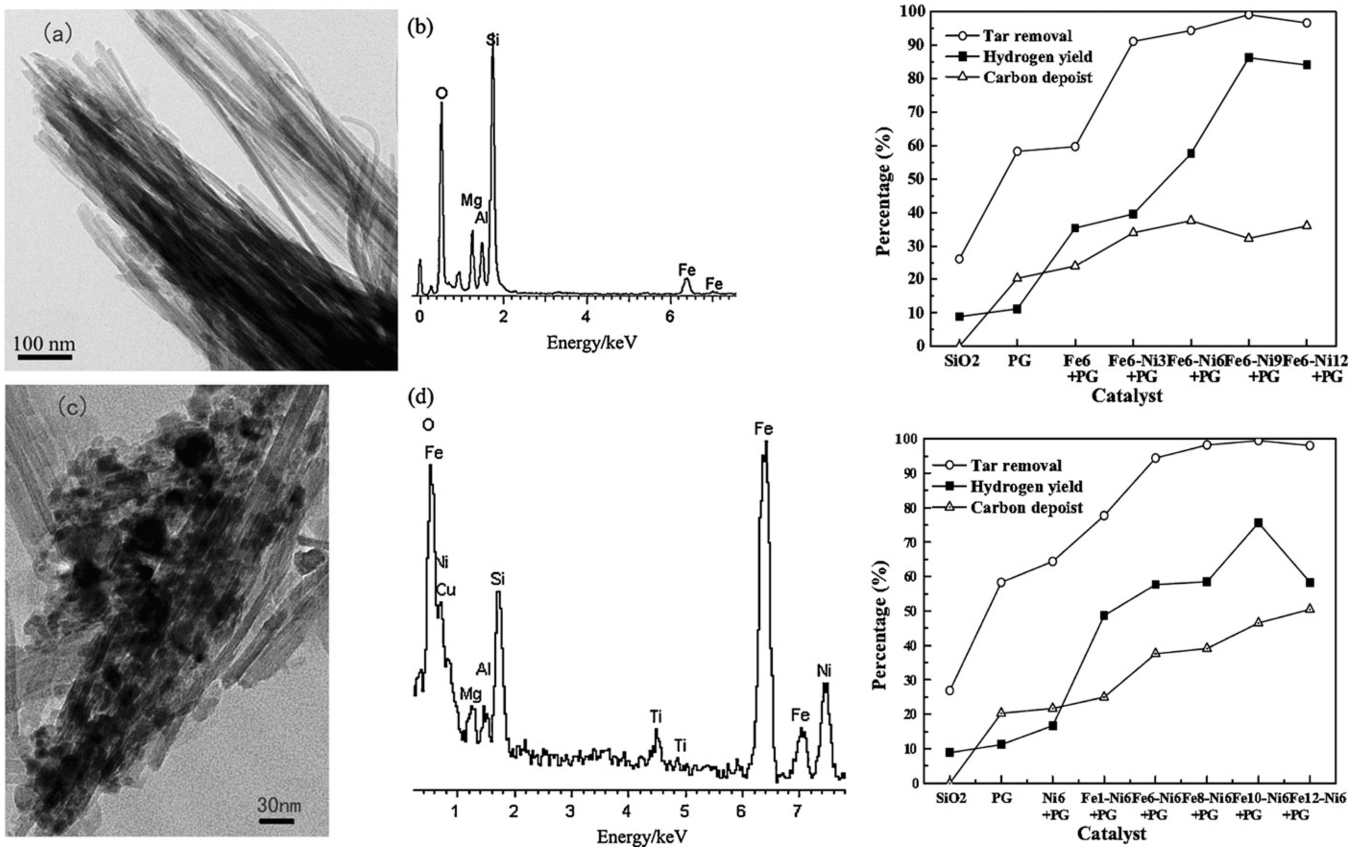


Fig. 4. HRTEM photographs and EDX spectra of the palygorskite and reduced catalyst: palygorskite ((a) and (b)), and ((c) and (d)) Fe_6–Ni_6/PG, and effect of different Fe or Ni loading on Ni_6/PG catalysts on catalytic cracking biomass tar [80].

the reactivity of catalyst. Therefore, Fe_6-–Ni_y/PG catalysts can have a better reactivity than Fe_x–Ni_6/PG catalysts for catalytic cracking of biomass tar to have more rich hydrogen in reacted products. Fig. 5 shows reaction routes during catalytic cracking of biomass tar over Fe–Ni/PG catalyst. It indicates that under the function of Fe-–Ni/PG, biomass tar can be converted into C, H_2, CO, CH_4 and light hydrocarbon, in which palygorskite mainly plays a role of carrier and the interaction between nickel/nickel oxide and iron/iron oxide is the crucial reactivity component.

The TEM images of palygorskite calcinated at 500 °C and Fe_6–Ni_6/PG prepared with incipient wetness impregnation and co-precipitation are presented in Fig. 6. The images indicate that some particles are observed on the Fe_6–Ni_6/PG catalyst compared to palygorskite. This is in good agreement with the corresponding XRD patterns. XRD patterns of Fe_6–Ni_6/PG prepared with incipient wetness impregnation and co-precipitation show the existence of alloy and/or spinel of Ni and Fe. However, as shown in Fig. 4(b) and (c), some larger particles (100–400 nm) are found on the sup-port prepared with incipient wetness impregnation than these (5–40 nm) on palygorskite prepared with co-precipitation. Some highly dispersed nanoparticles are observed on the palygorskite in Fig. 4(c). The dispersion of catalysts prepared with co-precipitation appears superior to that of catalysts prepared with incipient wetness impregnation. Fe plays an important role in catalytic cracking of biomass tar using Ni_6/PG catalysts. In Fig. 7, it is evident the tar conversion and H_2 yield increased in the presence of Fe_6–Ni_6/PG and Ni_6/PG catalysts compared with a quartz catalyst. On the other hand, the Fe additive precursor influences the increase in tar conversion and H_2 yield. In the case of the Ni_6/PG catalyst modified by Fe $(NO_3)_3 \cdot 9H_2O$, it is found that tar conversion and H_2 yield obtained the highest values of 94.4% and 57.7%, respectively.

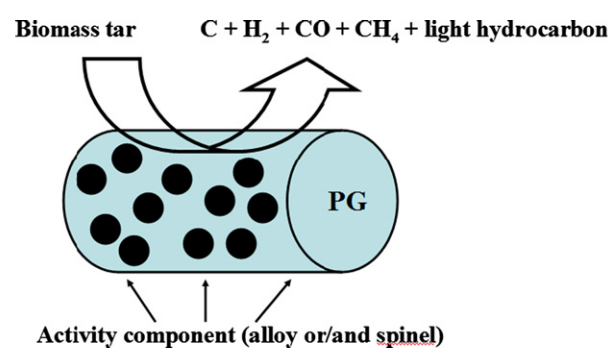


Fig. 5. Schematic of the catalytic cracking of biomass over Fe–Ni/PG catalyst.

2.1.3. *Nano-NiO/γ-Al_2O_3 catalyst*

As above saying, Ni-based catalysts are found to be the most popular types and also the very effective ones for hot gas cleaning. The developments of novel nickel-based catalyst with improved performance are being carried out. In recent years, nanomaterials have attracted extensive interests for their unique properties in various fields in comparison with their bulk counterparts [82,83]. Therein, nanometer-sized NiO (nano-NiO) particles have attracted much attention for their catalytic properties [84]. In particular, for saving cost, nano-NiO particles can be loaded on the surface of distinct carriers (such as alumina, Al_2O_3) to prepare the supported catalyst.

Li [85,86] developed a novel and low-cost nano-Ni catalyst on the support of γ-Al_2O_3, prepared by deposition-precipitation (DP) [87] method for tar removal in biomass catalytic gasification or pyrolysis. The TEM micrograph of NiO nanoparticles on catalyst surface is shown in Fig. 8(b). It can be seen that the NiO

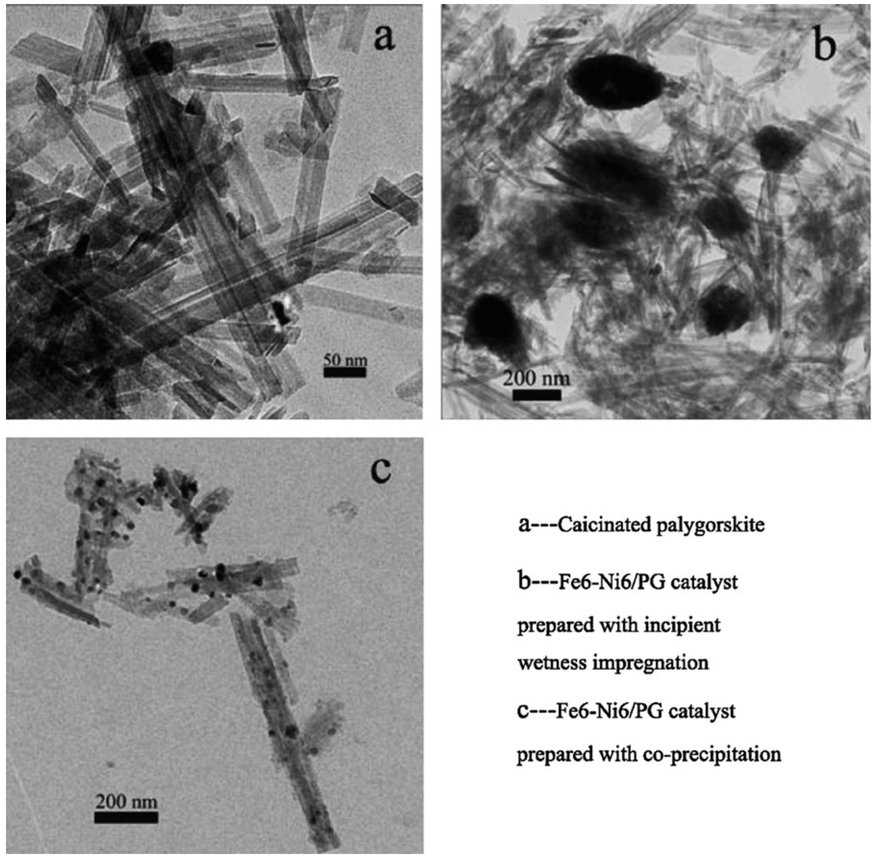


Fig. 6. TEM of PG and Fe_6–Ni_6/PG catalyst [81].

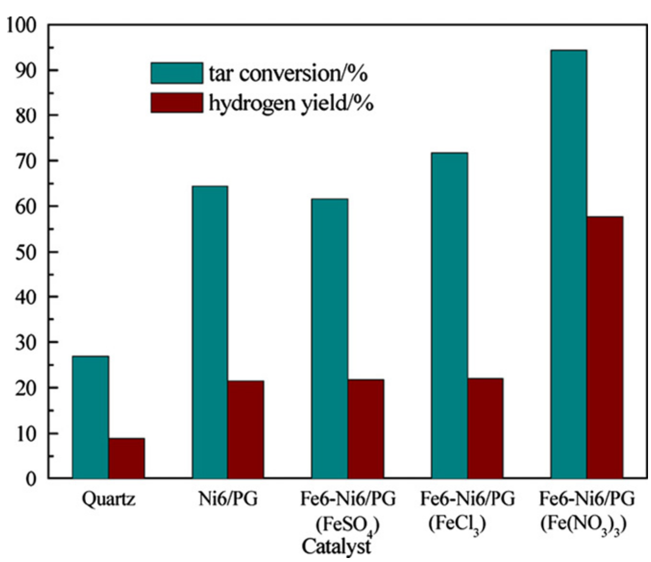


Fig. 7. Tar conversion and H_2 yield obtained from the catalytic decomposition of biomass tar with the Fe_6–Ni_6/PG catalyst as a function of the Fe additive precursor [81].

nanoparticles were sphere shaped. The size of nanoparticles was between 12 nm and 18 nm, which coincided with the XRD results (Fig. 8(c), the $NiAl_2O_4$ phase, which characterizes a spinel structure, appeared in the XRD profiles of catalyst samples) of catalysts. The SEM appearance image of NiO/γ-Al_2O_3 catalyst surface is shown in Fig. 8(b). The surface of catalyst was scraggy, the deposit of NiO nanoparticles on the surface of support was multilayer, and NiO nanoparticles displayed a fairly uniform spatial distribution on the surface.

The EDX analysis in Fig. 8(d) showed that the inside of catalyst consisted exclusively of the elements Al and O at 46.84% and 53.16%, respectively. But at the surface of catalyst three elements (Ni, Al, and O) were mainly observed at 52.04%, 5.44%, and 42.53%. This further confirmed that the prepared catalyst by DP method was a typical coated structure as eggshell, where the NiO nanoparticles mainly coated on the surface of γ-Al_2O_3 sphere. The core parts were γ-Al_2O_3, and the shell layers were enriched in NiO nanoparticles. Meantime, the above observations also indicated that no Ni was found inside the catalyst and that the main composition of catalyst surface was nickel oxide with few Al-bearing compounds that can be attributed to the interaction of NiO nanoparticles with alumina support [85].

Various nickel-based catalysts were reported in previous literatures for tar removal and improvement of the produced gas quality. For instance, a nickel-based catalytic filter was developed by Baron et al. [88] to achieve 99.0% tar conversions at optimal operating condition of 850 °C, but with only 77% tar reduction observed at 800 °C. A co-precipitated catalyst of Ni/Al for biomass catalytic pyrolysis was prepared with various pre-treatments, the resulting tar and gas yield was 2.7–7.3 wt% and 61.2–80.0%, respectively, at 700 °C pyrolysis temperatures [89]. Corella et al. [90,91] tested seven commercial Ni-based catalysts (NiO content of 12–25 wt%) and reported that they all showed to be very active, with about 95% tar removal easily obtained at 800–850 °C. However, their results were all based on crushed particles of the catalyst, for commercial application the effectiveness factors of 1–10% (only) might have to be applied. In this study, the tar removal efficiency exceeded 99% at 800 °C (Table 3), indicating that the prepared NiO/γ-Al_2O_3 catalyst was ideal for

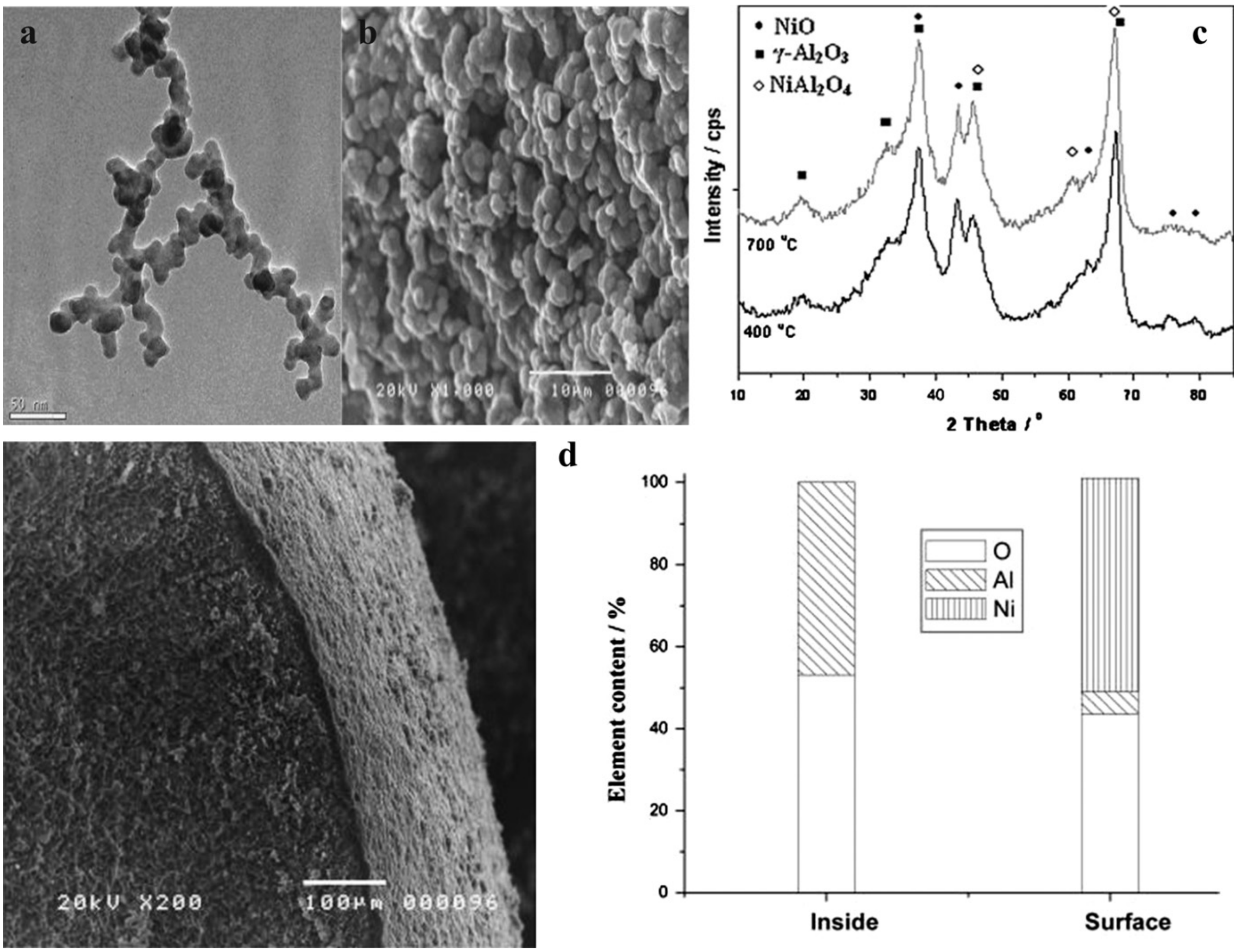


Fig. 8. (a) TEM, (b) SEM micrographs of nanoparticle on Nano-NiO/γ-Al_2O_3 catalyst, (c) XRD pattern of the catalyst samples calcined at 400 °C and 700 °C and (d) SEM cutaway photograph of NiO/γ-Al_2O_3 catalyst with EDX analysis [85].

tar removal in biomass pyrolysis with a high efficiency in comparison with the commercial and other nickel-based catalysts mentioned above. In catalytic pyrolysis with nano-NiO/γ-Al_2O_3 catalyst, the contents of H_2 and CO in gas increased significantly and also increased with the temperature of catalytic bed. They became finally the predominant gas components, with 49.2% H_2 and 42.2% CO generated at 800 °C. For an easy comparison, the gas product percentages with presence of commercial nickel-based catalyst were also listed in Table 3. It is clear that the nano-NiO/γ-Al_2O_3 catalyst demonstrated a better performance in improving gas product quality than the commercial one, with higher H_2 and CO but lesser CO_2 contents observed, even at a lower reaction temperature. The prepared nano-NiO/γ-Al_2O_3 catalyst could improve significantly the quality of the produced gas and remove efficiently tar presented in the vapor phase of biomass pyrolysis. Taking up to evaluate systematically the developed catalyst, the further study on catalyst lifetime, the possibility of quick deactivation and regeneration and the effect of various carriers would be performed in near future.

Furthermore, Li and his co-workers [92–94] studied on a supported tri-metallic catalyst (nano-Ni–La–Fe/γ-Al_2O_3) for tar removal in biomass steam gasification to significantly enhance the quality of the produced gas. Compared with the supported nano-NiO/γ-Al_2O_3 catalyst under the same conditions, the addition of lanthanum (La) and iron (Fe) to the nano-NiO/γ-Al_2O_3 catalyst resulting in a minor increase in CO, CO_2, CH_4, C_2 and total gas yield, while the H_2 yield remained almost unchanged [92]. This demonstrated that with nano-Ni–La–Fe/γ-Al_2O_3 catalysts, there was higher transformation of the carbon contained in the biomass to valuable gases, and consequently less coke was formed over the catalyst.

2.1.4. *Nanoarchitecured Ni_5TiO_7 catalyst*

Because of their high specific surface area, the use of nanomaterials is a popular path in order to achieve the highest functional efficiency as catalytic material. Jiang [95] succeeded in the synthesis of a further member of the compound nanowire family utilizing a solid reaction of NiO with a porous and atomically rough TiO_2 surface that has been produced by plasma oxidation. The novel nanoarchitectured $Ni_5TiO_7/TiO_2/Ti$ compound composite as a catalyst in a biomass gasification process have proven outstandingly active as catalysts and appear most suitable for high-temperature operation in biomass gasification featuring high efficiency and long-term stability. This finding is of great interest for gasification of biomass in the context of energy generation and may pave the way to an improved and environmentally friendly technology. The increased specific surface of the architectured nanowires, compared to common coated spherical geometries, enhances naphthalene conversion. For the application as a downstream catalyst, the examined material appears very suitable, in terms of conversion efficiency and durability.

Table 3
Product yields (wt%, daf. as received) and gas composition (vol%) from pyrolyzing Sawdust with and without catalyst.

Conditions	Product yields (wt%, daf)				Gas composition (vol%)					
	Gas	Tar	Water	Char	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6
Primary prolysis without catalyst at 800 °C	62.9	18.2	7.1	11.8	18.8	22.3	39.3	16.5	2.6	0.5
Catalytic pyrolysis with NiO/γ-Al_2O_3 catalyst										
600 °C	77.8	1.9	8.4	11.9	42.3	22.5	27.6	6.1	1.1	0.4
700 °C	80.9	0.8	6.5	11.8	45.1	33.6	16.7	3.7	0.7	0.2
800 °C	85.2	0.2	3.0	11.6	49.2	42.2	5.9	2.1	0.5	0.1
Catalytic pyrolysis with commercial catalyst										
600 °C	71.4	7.6	9.2	11.8	37.0	21.6	30.9	8.7	1.4	0.4
700 °C	78.1	3.3	6.8	11.8	42.6	27.8	22.5	5.8	1.0	0.3
800 °C	82.5	1.6	4.2	11.7	45.5	36.1	14.2	3.4	0.7	0.1

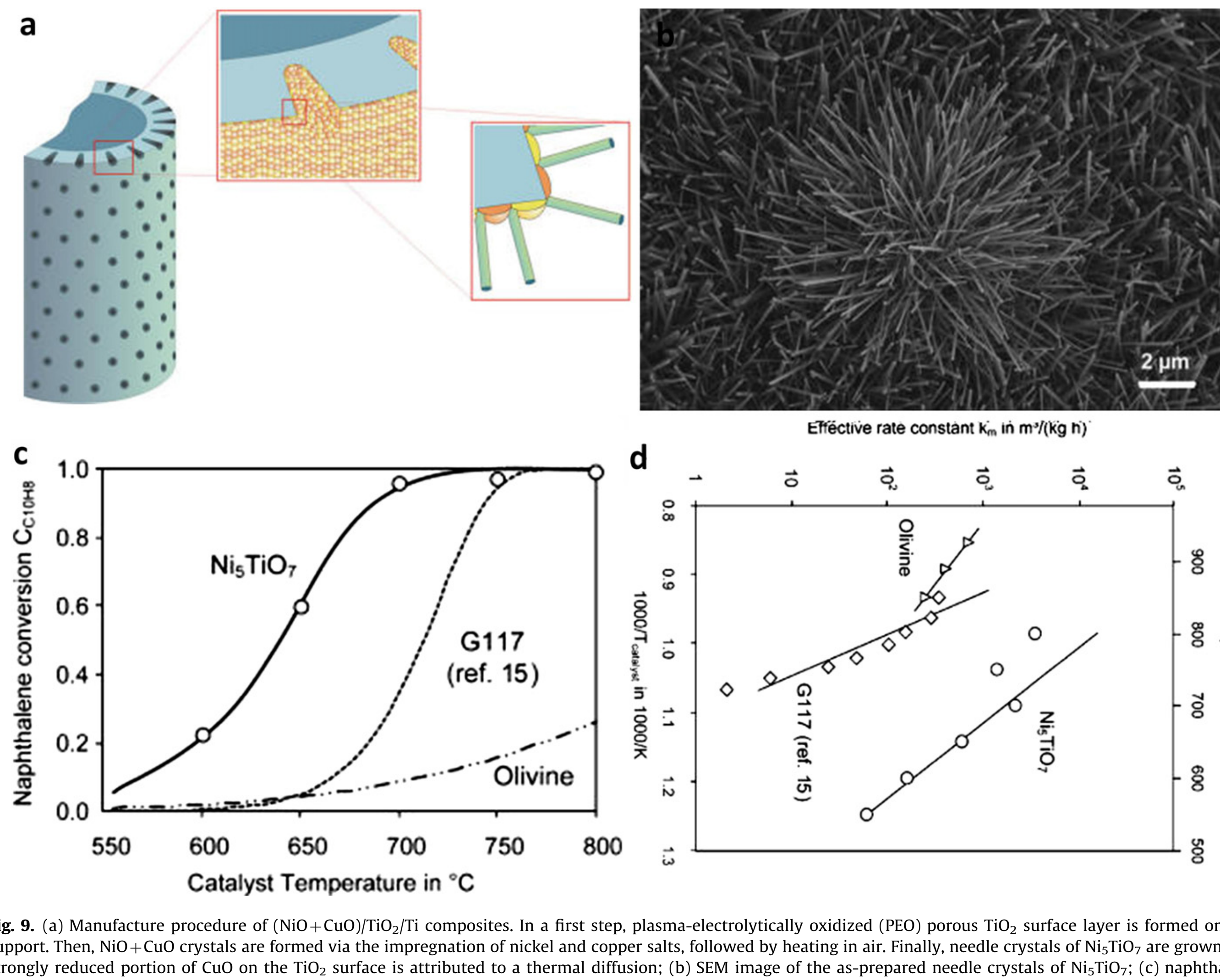


Fig. 9. (a) Manufacture procedure of (NiO+CuO)/TiO_2/Ti composites. In a first step, plasma-electrolytically oxidized (PEO) porous TiO_2 surface layer is formed on a Ti support. Then, NiO+CuO crystals are formed via the impregnation of nickel and copper salts, followed by heating in air. Finally, needle crystals of Ni_5TiO_7 are grown. The strongly reduced portion of CuO on the TiO_2 surface is attributed to a thermal diffusion; (b) SEM image of the as-prepared needle crystals of Ni_5TiO_7; (c) naphthalene ($C_{10}H_8$) conversion on G117 commercial Ni-catalyst (dotted line), on olivine (dash-dotted line), and on Ni_5TiO_7/TiO_2/Ti compound system (empty circles are data points; trend is represented by the solid line). Residence time with respect to the empty reactor: 1.0 s (20 °C); atmospheric pressure; gas composition at reactor inlet: 1.7 vol% $C_{10}H_8$, 30 vol% H_2O, and balance N_2 and (d) $C_{10}H_8$ conversion on (◇) G117 commercial Ni Catalyst, (Δ) olivine, and (○) Ni_5TiO_7/TiO_2/Ti compound system. Residence time with respect to the empty reactor: 1.0 s (20 °C); atmospheric pressure; gas composition at reactor inlet: 1.7 vol% $C_{10}H_8$, 30 vol% H_2O, and balance N_2 (modified) [95].

Outstanding catalytic properties for the steam reforming of naphthalene could be shown with a high stability even after 100 cycles of loading for 1 h with subsequent combustion of the coke residues arising from the reform. The gas yields of H_2, CO, and CH_4 in the reforming of naphthalene in the temperature range of 700–900 °C have been increased significantly by more than a factor of 2, compared to a commercial catalyst (G117, Südchemie AG, Munich, Germany) and olivine catalyst (see Fig. 9(c)) [96]. It is supposed to be particularly important for future applications in the areas of gas cleaning and appropriate upgrading in the context of gasification of biogeneous and refuse-derived fuels. Meanwhile, from Fig. 9(d), it can assume that

different catalysts can be compared concerning the temperature dependency of naphthalene conversion in an Arrhenius' plot in accordance with the first-order kinetic approach (Eq. (16)) with an effective conversion rate constant $k_{m,\ tar}$. The first-order kinetic equation is as follows:

$$C_{\text{gravimetric}} = \frac{m_{tar,in} - m_{tar,out}}{m_{tar,in}} \tag{15}$$

where $m_{tar,in}$ is the mass of tar evaporated and fed into the catalyst reactor and $m_{tar,out}$ is the mass of the solid residues determined by gravimetric analysis of the gas scrubbing solvent in the tar sampling impinge train.

$$k_{m,tar} = -\left[\frac{\text{In}(1 - C_{\text{gravimetric}})}{\tau}\right] = k_{m,tar,0}\exp\left(-\frac{E_{A,tar}}{RT_{cat}}\right) \tag{16}$$

where $\tau = m_{cat}/V_{eff}\ (T_{cat})$, $k_{m,tar}$=conversion rate constant (in m^3/(kg$_{cat}$ h)), $k_{m,tar,0}$=frequency factor (in m^3/(kg$_{cat}$ h)), τ=residence time (in (kg$_{cat}$ h)/m^3), m_{cat}=mass of catalyst (in kg), $V_{eff}(T_{cat})$= volumetric gas flow in m^3/s.

2.2. Olivine catalysts

A large number of investigations deal with biomass gasification in fluidized bed reactors utilizing nickel based catalysts, dolomite or olivine. Supported nickel-based catalysts with various supports and promoters have been the most widely studied class of materials. The high activity and selectivity of those reforming catalysts is well known [97,98], but they are susceptible to deactivation from contaminants.

Olivine is a mineral containing magnesium, iron and silicon. In parallel with this research, some research groups have been investigating olivine as a tar removal catalyst [99–103] Rapagnà et al. [99] investigated the catalytic activity of olivine and observed that it has a good performance in terms of tar reduction and the activity is comparable to calcined dolomite. They reported more than 90% reduction in average tar content. The tar amounted 2.4 gm_0^{-3} compared to 43 gm_0^{-3} with only sand. Whereas Courson et al. [100] reported that olivine alone dose not show any activity for methane reforming. They prepared Ni–olivine catalyst by impregnation of natural olivine with an excess of nickel salt solution [101]. The catalyst was then calcined under air for 4 h at different calcination temperatures of 900–1400 °C. They reported that this Ni–olivine catalyst is active for dry reforming of methane.

Olivine consists mainly of silicate mineral in which magnesium and irons cations are set in the silicate tetrahedral [99]. Natural olivine is represented by the formula $(Mg,Fe)_2SiO_4$. The catalytic activity of olivine for tar elimination can be related to the magnesite (MgO) and iron oxide (Fe_2O_3) contents, where the latter is much higher in olivine than in dolomite. On this basis, the reactions involved in tar elimination with olivine should be similar to those involved in the same process with calcined rocks. This catalyst is mainly deactivated by the formation of coke, which covers the active sites and reduces the surface area of the catalyst. The advantages of this catalyst are its low price (similarly to dolomite) and high attrition resistance compared to dolomite. Its mechanical strength is comparable to that of sand, even at high temperatures. Its performance is therefore better than that of dolomite in fluidized-bed environments [99].

Olivine shows a slightly lower activity in biomass gasification and tar reforming, but higher attrition resistance than dolomite [99]. The addition of some metals to olivine can help to increase its tar reforming activity. In this sense, the tar abatement activity of a Ni/olivine catalyst was successfully demonstrated in the 100 kWth FICFB (dual fluidized bed steam blown biomass gasifier) pilot plant located in Vienna, with an order of magnitude reduction in the tar content of the product fuel gas [104,105]. The main drawback attributed to the use of Ni is the cost and the environmental and safety measures derived from its toxicity. In addition, Rauch et al. [106] demonstrated that olivine activity, or more specifically olivine activation, depends on its iron oxide content. In fact, depending on olivine temperature treatment, iron can be present in the olivine phase, or as iron oxides. Thus, iron impregnation of natural olivine appears to be very interesting way to produce in-bed primary catalysts, for both economic and environmental reasons. Iron does not affect the catalyst cost due to its low price in comparison to noble metals and nickel thus markedly reducing catalyst pollution problems.

Virginie [107] studied Fe/olivine on tar removal during biomass gasification in a dual fluidized bed. And the Fe/olivine catalyst efficiency was evaluated in biomass gasification in a dual fluidized bed for the production of a rich syngas and with low tar content. It has been found that Fe/olivine material has a double effect on tar destruction. On the one hand, it acts as a catalyst for tar and hydrocarbon reforming. On the other hand, it can act as an oxygen carrier that transfers oxygen from the combustor to the gasifier, and part of the oxygen is used to burn volatile compounds [107]. Therefore, an inexpensive and non-toxic Fe/olivine catalyst is a material suitable for use as a primary catalyst in a fluidized bed gasification of biomass and improves the commonly used olivine catalytic activity.

Meanwhile, the results indicated that the iron distribution in the samples after gasification shows a balance between the phases FeO and Fe_3O_4, which provide for tar reforming. Those iron species take place in the redox equations of the water gas shift reaction (Eqs. (17) and (18)):

$$Fe_3O_4 + CO \leftrightarrow CO_2 + 3FeO \tag{17}$$

$$3FeO + H_2O \leftrightarrow H_2 + Fe_3O_4 \tag{18}$$

In the previously stated conditions, the couple $Fe^{2+/3+}/Fe^{2+}$ is sufficiently efficient in tar reforming, without the presence of FeO. Several researches based on tars cracking from pyrolysis, from biomass gasification [108,109] or based on tar models molecules steam reforming [110–112], in the presence of iron catalysts, have different views on the most active iron oxidation state: FeO, Fe^{2+} or $Fe^{2+/3+}$.

Rapagnà [113] proposed Fe/olivine catalyst for biomass steam gasification, and investigated its characterization at real process conditions. When 10 wt% Fe/olivine is utilized in the gasifier, the gas yield increases on average by 40% and the hydrogen yield by 88%. Correspondingly, the methane content in the syngas is reduced by 16% and tar production per kg of dry ash free (daf.) biomass by 46%. 10 wt% Fe/olivine characterization after test shows that the catalyst is fairly stable. As shown in Fig. 10(B), H_2 concentration keeps an almost constant value in tests II–IV, equal to about 53% by volume (dry, N_2 free gas), resulting in an average enhancement in molar concentration of 36% in comparison to test I (Fig. 10(A)). No noticeable improvements have been achieved in test IV, performed at higher concentration of reactants. Fig. 10(C) compared 10 wt% Fe/olivine catalyst synthesized at laboratory scale with three different 10 wt% Fe/olivine catalysts synthesized in large scale. Olivine ($(Mg,Fe)_2SiO_4$) structure is the major crystalline phase for the iron catalysts. The presence of an enstatite phase ($MgSiO_3$) at $2\theta = 31.1^\circ$ is due to the reaction of amorphous silica with MgO [114]. Those phases are observed for the three different samples of the large scale synthesis involving homogeneity in the catalyst preparation. The similar patterns of the large and laboratory scale catalysts involve repeatability of the synthesis. With tests performed with a 10 wt% Fe/olivine

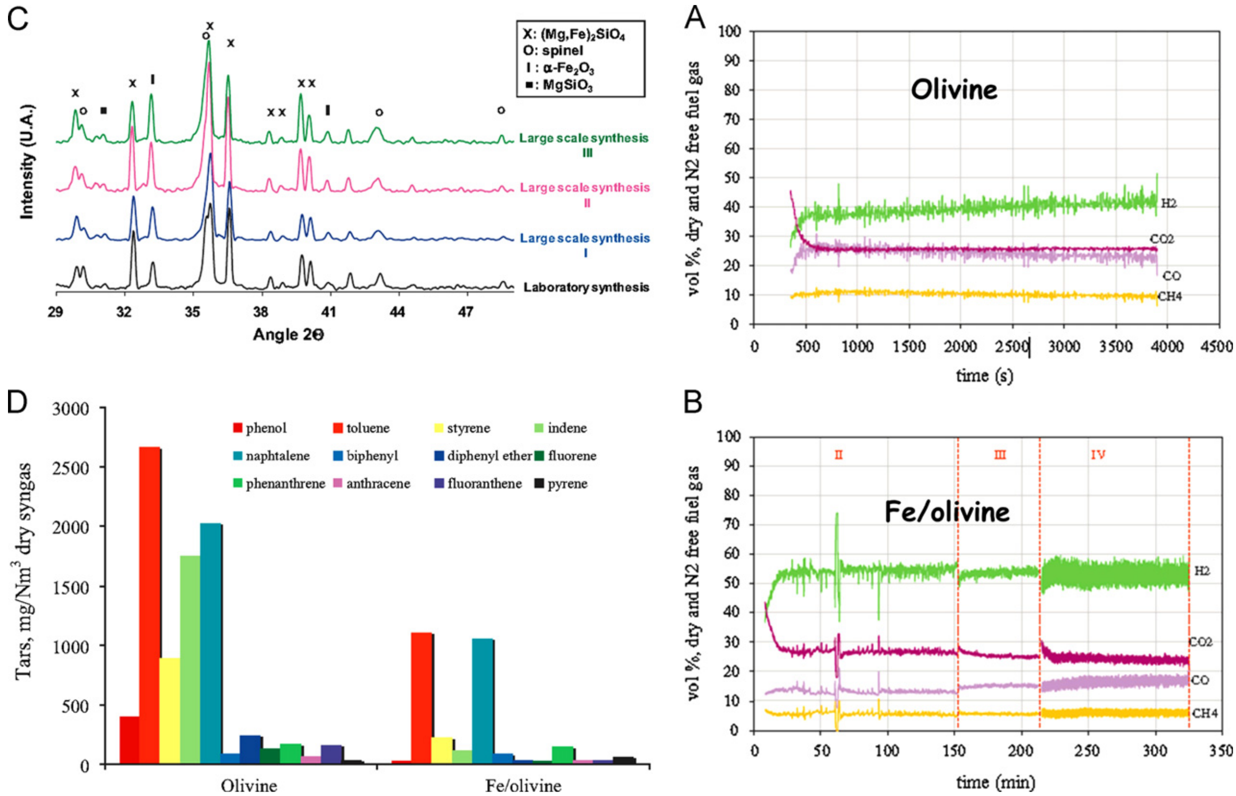


Fig. 10. Product gas composition in % by volume (dry, N_2 free gas) as a function of gasification time, when the fluidized bed in the gasifier is made of olivine particles (A—test I), or of 10 wt% Fe/olivine particles (B—tests II–IV); XRD diffractograms of 10 wt% Fe/olivine samples prepared by large scale synthesis, and synthesized in laboratory, respectively (C); Characterization of tar samples obtained from biomass gasification with olivine (I—reference test) and with 10 wt% Fe/olivine tests (D). (Modified) [113].

particle bed in the gasifier, the content of tar is well below that measured in the reference test. In this case, naphthalene and toluene, which are considered quite refractory to cracking/reforming reactions, decrease by 48% and 59% on average, respectively. The experimental evidence confirms that the iron impregnation of natural olivine leads to a promotion of reforming activity and a coherent decrease of tar concentration (Fig. 10(D)).

The temperature profile recorder (TPR) curve of the catalyst after gasification (Fig. 11) indicates a peak of hydrogen consumption between 500 °C and 700 °C which corresponds to the reduction of iron oxide in strong interaction with olivine structure. However, compared to the TPR curve of the 10 wt% Fe/olivine catalyst before test, a decrease in the hydrogen consumption is observed. This can be explained partly by the presence of iron in an oxidation state less than that prevailing initially (Fe_3O_4 ($Fe^{2.5+}$) instead of Fe_2O_3 (Fe^{3+}) before test) which needs less hydrogen to be reduced to metallic iron (FeO). However, a loss of iron added on olivine (about 5 wt% of total iron) during fluidization because of particle attrition phenomena, could mainly explain the decrease of hydrogen consumption [113]. In conclusion, the iron impregnation of natural olivine leads to improvement of tar elimination and promotion of reforming activity.

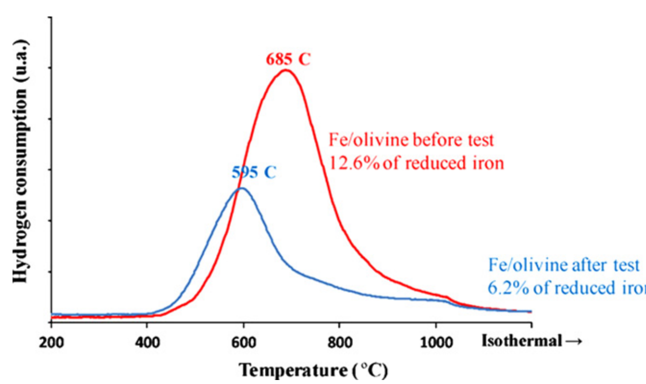


Fig. 11. TPR profiles of 10 wt%Fe/olivine: before test; after biomass gasification [113].

2.3. Dolomite catalysts

Increasing the Ca/Mg ratio, decreasing the grain size, and increasing the active metal content such as iron can improve the activity of these catalysts [115]. Ca improved the formation of crystal structure and Mg enhanced the degree of carbon structure ordering which played a negative role in gasification. On the other hand, Ca metal cannot be used as a catalyst at high temperature, because its particles are inclined to agglomerate, resulting in deactivation [116]. Influence of alkaline earth metal oxides (CaO and MgO) on steam gasification of biomass was studied by Xie et al. [117]. They found that the catalysts mainly increased the yields of permanent gases (H_2, CO_2, etc.) and improved the quality of gaseous product by promoting the decomposition reactions of tar and light hydrocarbon (C_nH_m) and the gasification reaction of char.

Dolomite is a calcium magnesium ore with general chemical formula Ca, $Mg(CO_3)_2$, and is generally used as raw material in the manufacture of magnesium. In recent years, it has been discovered that calcined dolomite is also a highly efficient catalyst for removing tar from the product gases of gasifier. Norwegian dolomitic magnesium oxide (MgO) showed a higher catalytic decomposing activity on the tar-derived one-ring species toluene

than quicklime (CaO) [118]. In the experiment of Siedlecki et al. [119], magnesite showed activity in promoting the water–gas shift reaction, (steam) reforming of methane and C_2 hydrocarbons toward their equilibrium, and reducing the tar (toluene, xylenes, polycyclic aromatic hydrocarbons/PAHs, and phenolics). The concentration of PAHs and phenolics is reduced to 1.9 g/N m^3 (below 2 g/N m^3), being considered as an important limit for many downstream applications. However, the activity of CaO and MgO is still below CaO–MgO for tar elimination and gas yield in the following order: calcined dolomite (CaO–MgO) > calcined magnesite (MgO) > calcined calcite (CaO) [120].

The catalytic activity of calcined dolomite was extensively investigated in terms of tar reduction [120–131]. Calcined dolomite catalyst is more active than the un-calcined dolomite for tar decomposition since its large (internal) surface area and oxide contents on the surface. Hu et al. [132] compared a calcined dolomite with an un-calcined dolomite as well as a calcined olivine and raw olivine as downstream catalysts in steam gasification of apricot stone and found that among all the catalysts tested the calcined dolomite is the most effective catalyst for increasing the H_2 content in the gas.

The addition of calcined dolomite in the bed material improve the tar conversion [122–124,133], agreed with Corella et al. [134] who stated that the effectiveness of the dolomite in the second reactor is only a little bit higher than for the in-bed location as shown in Fig. 12. This small increase in effectiveness is mainly found in gasification with H_2O+O_2 mixtures and there is no chemical difference (between the two locations of the dolomite) in gasification with air. Addition of 17 wt% (pre-calcined) dolomite converted 90% PAHs and the total tar amount of 4.0 g/N m^3 could be reduced to 1.5 g/N m^3 [135]. With a 15–30 wt% of calcined dolomite in the bed, tar contents below 1 g/N m^3 can be obtained [122,123]. This in-bed tar elimination causes an increase in the H_2 content from 6–10 to 12–17 vol%, the CO content from 9–16 to 16–22 vol%, and the CH_4 content from 2.5–3.5 to 4.0–5.2 vol% [121].

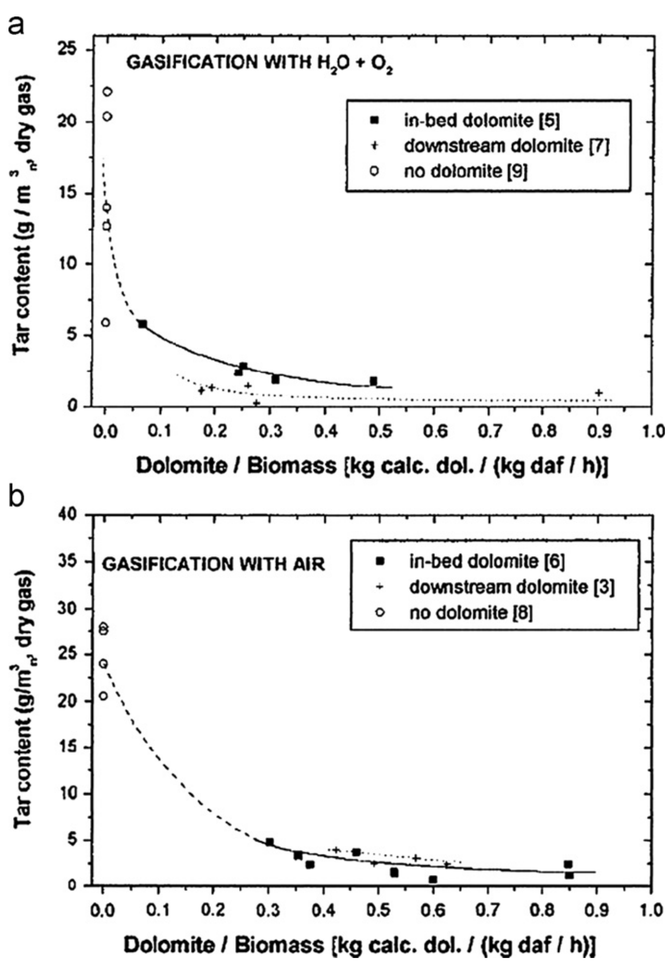


Fig. 12. Tar content in the flue gas versus relative amount of dolomite used for two locations of the dolomite and for two gasifying agents; (a) gasification with H_2O+O_2 mixtures, gasification ratio (GR)=0.86–1.16, T=820–840 °C and (b) gasification with air, equivalence ratio (ER)=0.22–0.26, T=800–850 °C [136].

Gusta et al. [124] reported that dolomites improved tar conversion to gaseous products by an average of 21% over noncatalytic results at a 750 °C isothermal catalyst bed temperature using 1.6 cm^3 dolomite/g of biomass. The iron content in dolomite was found to promote tar conversion and the water–gas shift reaction, but the effectiveness reached a plateau at 0.9 wt% Fe in Canadian dolomites. The maximum tar conversion of 66% was achieved at 750 °C using a Canadian dolomite with 0.9 wt% Fe (1.6 cm^3/g of biomass) and carbon conversion to gaseous products increased to 97% using 3.2 cm^3 dolomite/g of biomass at the same temperature. The dolomite seemed stable after 15 h cyclic use at 800 °C. In the experiment of Wang et al. [136], modified dolomite (mixed of natural dolomite and Fe_2O_3 powders) showed higher activity. Tar conversion ranged from 43% to 95% with calcined dolomite catalyst, and 44–97% with modified dolomite.

2.4. Zeolites catalysts

Zeolite, silica–alumina, etc. are the acid catalysts. Zeolites are crystalline silicates and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing channels and cavities of molecular dimensions [137]. Zeolites are solid catalysts with the following properties: (1) high surface area, (2) molecular dimensions of the pores, (3) high adsorption capacity, (4) partitioning of reactant/products, (5) possibility of modulating the electronic properties of the active sites, and (6) possibility for preactivating the molecules by strong electric fields and molecular confinement [137]. The acidic properties (Bronsted sites) of zeolites are depended on the method of preparation, form, temperature of dehydration, and Si/Al ratio. The key properties of zeolites are structure, Si/Al ratio, particle size, and nature of the (exchanged) cation. These primary structure/composition factors influence acidity, thermal stability, and overall catalytic activity [8].

Zeolites have been widely used in heterogeneous catalysis because of their well-defined pore structures and capabilities of extremely high surface area and surface acidity [138] and the most used in industrial applications [139] since its commercial availability [137]. The modification of acidic zeolites with dispersed metals produces catalysts suitable for hydrogenation and ring breaking reactions of aromatic hydrocarbons such as benzene, toluene, naphthalene, and polycyclic aromatics. The catalysts have relatively high tolerance for sulfur compounds in the context of clean up of gasification effluents [139]. In the case of tar reduction, various kinds of zeolites especially the commercial catalysts were tested by some researchers [140–153].

The advantages of zeolites are related to their acidity, better thermal/hydrothermal stability, better resistance to nitrogen and sulfur compounds, tendency toward low coke formation, and easy regenerability. The other advantages with zeolites are their relatively low-price and the knowledge gained about them from long experience with their use in fluid catalytic cracking (FCC) units. However, the main disadvantage with these catalysts is the rapid deactivation because of coke formation [8,142].

Nickel is the most widely used metal for steam reforming applications due to economic reasons and also has a relatively high activity compared with Co, Pt, Ru, and Rh [153,154]. Utilizing the advantages of using zeolites and nickel metal mentioned

above, Buchireddy [155] investigated the use of zeolites and nickel-supported zeolites as a potential tar removal catalyst. An increase in the SiO_2/Al_2O_3 ratio corresponds to a decrease in the acidity [155]. Hence, ZY-5.2 with a SiO_2/Al_2O_3 of 5.2 is more acidic compared to ZY-80 with a SiO_2/Al_2O_3 of 80. Fig. 13 shows that ZY-5.2 had the highest activity and SiO_2/Al_2O_3 had the least activity toward naphthalene conversion. This could be due to the higher acidity of zeolites compared with amorphous SiO_2/Al_2O_3. Zeolite catalysts are more active than amorphous catalysts due to their higher acidic strength both in terms of their strength and number of acid sites [156,157]. Also, it can be seen that naphthalene conversion increased from 33% to 55%, with a decrease in SiO_2/Al_2O_3 from 80 to 5.2 for ZY. This increase can once again be attributed to the higher acidity of ZY-5.2 compared with ZY-80. However, naphthalene conversion of Na-chabazite with a SiO_2/Al_2O_3 of 4.0 was lower than ZY with a SiO_2/Al_2O_3 of 80. This could be due to the presence of sodium, which neutralizes the acidic sites on chabazite. The intensity of darkness increased from ZY-80 to ZY-5.2 (Fig. 13). This could be due to an increase in coke formation with an increase in the acidity of the catalyst.

As shown in Fig. 14(A), nickel-supported catalysts had a significant improvement in activity toward naphthalene conversion for all the zeolites tested. Naphthalene ($C_{10}H_8$) conversion improved significantly from 13% to 87% and 33% to 98% for SiO_2/Al_2O_3 and ZY-80, respectively, with the impregnation of nickel. The improved performance of nickel-supported zeolites is attributed to the steam and dry reforming activity of impregnated nickel as shown in Eqs. (19) and (20).

$$C_{10}H_8 + 10H_2O \leftrightarrow 10CO + 14H_2 \quad (19)$$

$$C_{10}H_8 + 10CO_2 \leftrightarrow 20CO + 4H_2 \quad (20)$$

Fig. 14(A) also shows that the activity of nickel-supported zeolites increases with a decrease in the zeolites' acidity. Naphthalene conversions reported were 78% and 99% for Ni/ZY-5.2 and Ni/ZY-80, respectively. In contrast, the activity of zeolites decreased with a decrease in the acidity. This anomaly could be attributed to the coke formation on the catalyst surface. Coke formation increases with an increase in acidity, as discussed earlier. Since Ni/ZY-5.2 is more acidic, the ability of coke formation is greater compared with Ni/ZY-80.

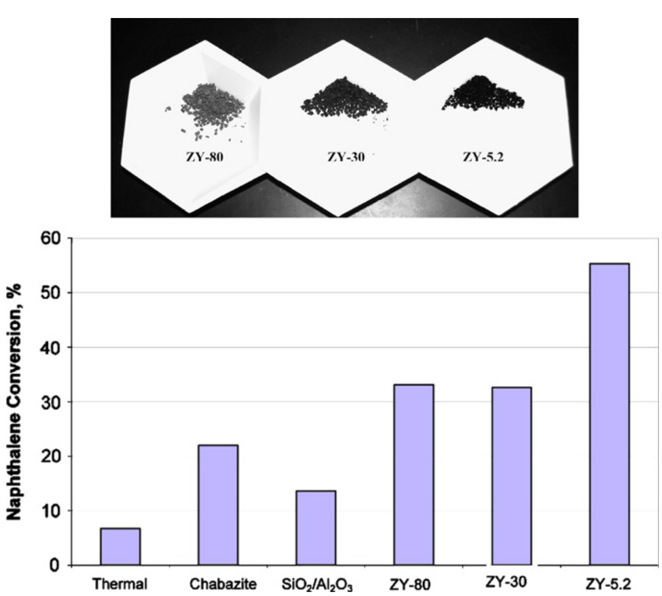


Fig. 13. Variation of naphthalene conversion with SiO_2/Al_2O_3 of zeolites (T, 750 °C; S/C, 5.0; GHSV, 12,800 h^{-1}; naphthalene loading, 12 g/N m^3).

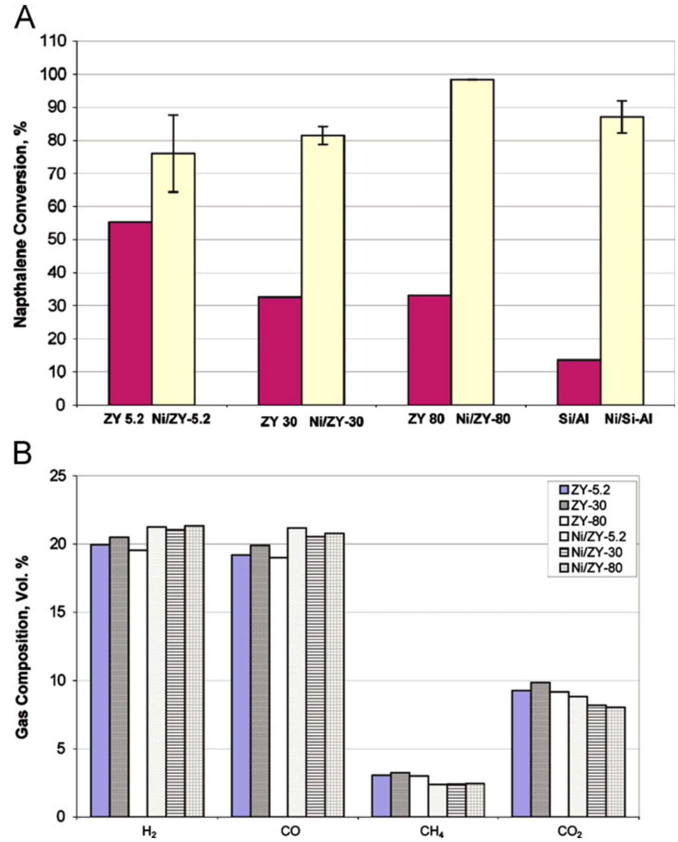


Fig. 14. (A) Variation of naphthalene conversion and (B) product gas composition (initial gas composition: H_2, 20%; CO, 20%; CO_2, 9%; CH_4, 3%) with zeolites and nickel supported zeolites catalysts (T, 750 °C; S/C, 5.0; GHSV, 12,800 h^{-1}; naphthalene loading, 12 g/N m^3) [155].

Variation of exit gas composition with the different zeolites tested is presented in Fig. 14(B). These gas samples were collected at the end of the experimental run. These exit gas composition variations are due to several thermodynamically favorable reactions occurring in series and/or parallel. Fig. 14(B) shows that the H_2 and CO content is higher for Ni/zeolites (H_2, 21–21.3%; CO, 20.5–21.2%) compared with the zeolites (H_2, 19.5–20.5%; CO, 19–19.9%). This increase in the H_2 and CO contents is attributed to the presence of nickel metal on the zeolites. Since Ni is a good steam and dry reforming catalyst, naphthalene conversions increase for Ni/zeolites as shown in Fig. 14(A). This increase in naphthalene conversions via Eqs. (19) and (20) might have increased the CO and H_2 content of the exit gas. Moreover, a decrease in the methane and CO_2 compositions is observed for Ni/zeolites compared with those for zeolites. This decrease could be attributed to the methane reforming and reverse water gas shift activity, as shown in Eqs. (21)–(22).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (21)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (22)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (23)$$

In summary, Nickel-supported zeolites have a very high tar removal potential. Long-term activity tests showed that Ni/ZY-80 and Ni/ZY-30 achieved naphthalene conversions of greater than 99% with very little loss of activity at the end of the 97 h test duration. The activities of Ni/ZY-5.2, Ni/Si–Al, and Ni/chabazite decreased over time, and the decrease in activity was associated with coke deposition and a loss of active surface area.

2.5. Ceramic catalysts

The required reaction temperatures for effective catalytic tar reforming range from 750 °C to 850 °C [158–164]. At this high temperature silicon carbide is the hot gas filter material of choice due to its high thermal and especially thermoshock resistance. Catalytic tar reforming hot gas filter elements can be produced by using a special design of a cylindrical catalytic filter element with a porous cylindrical inner tube and filling a tar reforming catalyst into the hollow cylindrical space between the filter element and the inner tube as shown in Fig. 15 [165]. The catalytic performance of this design up to the prototype scale was already described in detail in previous work [165]. The main advantage of this design is the flexibility to integrate the tailor-made tar of 1.5 higher than the face velocity related to the outer surface of the catalytic filter element caused by the cylindrical design of the catalytic filter element. With regard to a simplification of the manufacturing process of tar reforming catalytic filter elements and to apply a higher face velocity to reduce the size of the catalytic filter, an alternative integration of the catalyst in the hot gas filter element as catalytic layer by catalytic activation of the 10 mm thick porous silicon carbide filter element would be desirable (Fig. 15). Silicon carbide-based filter elements proposed by Nacken [166,167] were catalytically activated to provide filter elements for catalytic tar removal from biomass-derived syngas. The filter element support was coated with CeO_2, $CaO–Al_2O_3$ and MgO with a specific surface of 7.4 m^2/g, 15.9 m^2/g and 21.9 m^2/g synthesized by exo-templating with activated carbon. An increase of the NiO loading from 6 wt% to 60 wt% on an MgO coated filter element resulted in an increase of the naphthalene conversion from 91% to 100% at 800 °C and a face velocity of 2.5 cm/s at a naphthalene concentration of 5 g/N m^3 in model biomass gasification gas. In case of an $MgO–Al_2O_3$ coated filter element with 60 wt% NiO in addition to complete naphthalene conversion in the absence of H_2S, a higher conversion of 66% was found in the presence of 100 ppmv H_2S compared to 49% of the MgO–NiO coated filter element. After scaling up of the catalytic activation procedure to a 1520 mm long filter candle, which shows an acceptable differential pressure of 54.9 mbar, 58% and 97% naphthalene conversion was achieved in the presence and absence of H_2S, respectively.

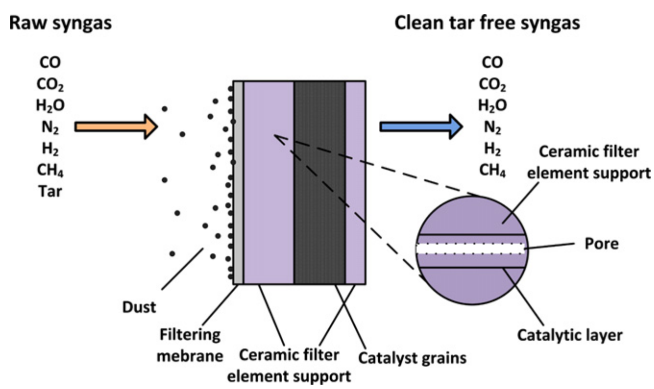


Fig. 15. Schematic design of a tar reforming catalytic filter element with integrated fixed bed and catalytic layer [165].

2.6. Other catalysts

2.6.1. Non-Ni based catalysts

As we know, Ni based catalysts have some disadvantages of secondary pollution and short term catalytic activity. Supported Co catalysts have been utilized recently for the steam reforming of oxygenates and hydrocarbons such as ethanol [168], methanol [169], naphthalene [170,171], biomass tar [78,172,173] and wood char [174] and so on, and performance of Co catalysts has been reported to be comparable to that of Ni catalysts [175–178]. The modification of Co/Al_2O_3 with Fe is attempted. This is because Fe can interact with Co to form Co–Fe alloy, and the synergy between two components with different oxygen affinity is also expected. On the other hand, supported Co catalysts modified with Fe addition have been utilized recently for the steam reforming of oxygenates, such as ethanol [179–183], acetic acid [184] and alcohol [185], and Fischer-Tropsch synthesis [186–190]. Wang [191] investigated the performance of $Co–Fe/Al_2O_3$ catalysts prepared by co-impregnation method in the steam reforming of tar derived from the pyrolysis of cedar. In addition, the performance of the catalysts in the steam reforming of toluene as one of aromatic model compounds of tar was also tested. From the results of these tests and characterization of catalysts before and after the catalytic use, it is found that the bcc Co–Fe alloy particles are important for high catalytic activity.

In the research of Wang et al. [191], Fig. 16 shows the catalytic performance of $Co–Fe/Al_2O_3$, Co/Al_2O_3 and Fe/Al_2O_3 in steam reforming of tar at 823 K. In the case of Fe/Al_2O_3, the amount of the residual tar was large and the ratio of H_2 to CO (H_2/CO) was rather low, indicating the low reforming activity of Fe/Al_2O_3. The addition of Fe to Co/Al_2O_3 decreased the amount of tar in the range of the molar ratio of Fe to Co (Fe/Co) ≤ 0.25, and this means that Fe addition promoted the steam reforming of tar. When the

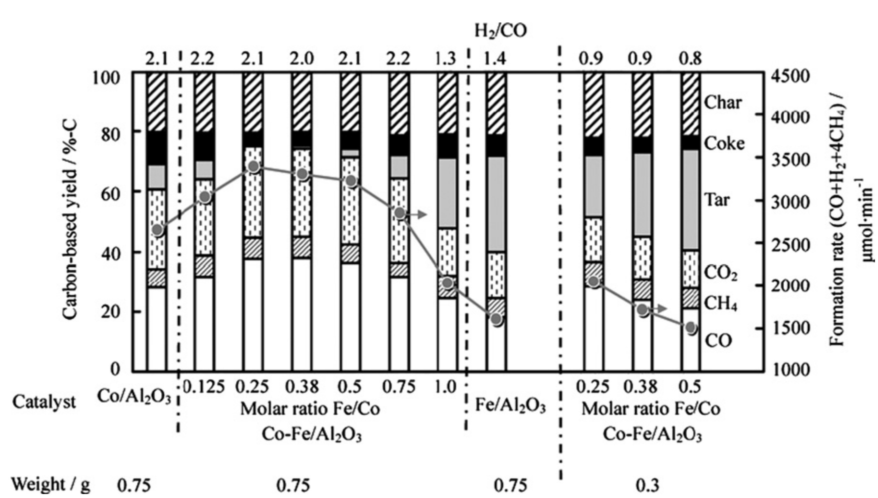


Fig. 16. Catalytic performance in steam reforming of tar over $Co–Fe/Al_2O_3$ catalysts at 823 K [191].

0.75 g catalyst was used, almost all of tar was converted over the catalysts with Fe/Co=0.25, 0.38 and 0.5. In order to optimize the Fe amount more precisely, the catalysts were also tested with 0.3 g of catalysts (Fe/Co=0.25, 0.38, 0.5). As a result, it is concluded that Co–Fe/Al_2O_3 (Fe/Co=0.25) was optimum, and the addition of Fe at the optimum amount enhanced the reforming activity and decreased the coke amount. The excess addition of Fe (Fe/Co > 0.5) decreased the catalytic performance significantly. This behavior is similar to the dependence of the additive amount of Fe over Ni–Fe/Al_2O_3 on the catalytic performance in the steam reforming of tar in the previous report [192], although the optimum amount of Fe on Co/Al_2O_3 was different from that on Ni/Al_2O_3 (Fe/Ni=0.5).

2.6.2. *Carbon-supported catalysts*

Activated carbon (AC) is a non-graphitic, microcrystalline form of carbon. Its structure is more disordered than that of graphite, and contains crystallites only a few layers thick and less than 10 nm wide [193]. The porous areas between the crystallites constitute the large surface area of the activated carbon. The porosity can vary from micropore (< 2 nm), to mesopores (2–50 nm) to macropore (> 50 nm). These pores contribute to the large internal surface areas and pore volumes of activated carbons and can range from 250 m^2/g to 2500 m^2/g and 0.1 ml/g to 1.0 ml/g, respectively [193,194]. Due to their highly porous textural structures (Fig. 17) [195], activated carbons or charcoals (derived from biomass or coal) have also been widely used as catalyst supports for conversions of hydrocarbons and tar cracking, not only because their macropores and mesopores would greatly improve the dispersion of metal ions, but facilitate transport of reactant molecules (e.g., toluene, 0.68 nm molecular size) into the internal surfaces of the catalyst, as illustrated in Fig. 18(A). It has been demonstrated that activated carbon has a high affinity and adsorption selectivity to hydrocarbon compounds such as asphaltenes [196,197]. Particularly the mesopores of the activated carbon was thought to play an important role for effective conversion of heavy hydrocarbon compounds into lighter fractions, while restricting the carbon/coke formation [169,171]. In addition, carbon-supported catalysts, due to their neutral or weak base properties, were found to be superior to the solid acid catalysts with respect to the resistance to deactivation by deposition of coke and heavy metals [194,196].

In the experiment of Xu [195], the Ni–Mo–BAC (biomass derived activated carbon) catalyst proved to be superior to the Ni–Mo/BAC in that during the course of hydro-treating Athabasca vacuum tower bottoms (AVTB), the porous textural structure of the Ni–Mo–BAC catalysts remained better than that of Ni–Mo/BAC, leading to a larger total pore volume (0.4 cm^3/g) and greater BET surface area (455 m^2/g) for the spent catalyst, compared with 0.12 cm^3/g pore volume and 150 m^2/g BET surface area for the spent Ni–Mo/BAC. Furthermore, the TEM measurement for the fresh catalyst Ni–Mo–BAC indicated the presence of highly dispersed nanoparticles (20–50 nm) of Ni, Mo metals, as illustrated in Fig. 18(B). The highly dispersed metallic nanoparticles in the highly porous carbon matrix could effectively act as the active adsorption sites for both the solvent and the polycyclic aromatic asphaltene compounds, which would promote the Hydro-deasphalting (HDAs) reactions in accordance with the mechanism as proposed in Fig. 19.

Abu et al. [198] compared the activity of a biomass char to other catalysts that are commonly used for tar decomposition, including calcined dolomite (21 wt% MgO, 30 wt% CaO, 0.2 wt% Fe_2O_3), olivine (50 wt% MgO, 42 wt% SiO_2, and 7 wt% Fe_2O_3), and a nickel catalyst (70 wt% NiO, 12 wt% Al_2O_3 and 7 wt% SiO_2). The biomass char was produced by pyrolysis of pinewood at 500 °C. Phenol (8–13 g/N m^3) and naphthalene (40 g/N m^3 or 90 g/N m^3) were used as tar models and the tests were carried out in the presence of CO_2 (6 vol%), H_2O (10 vol%) and N_2 (balance) at 700 °C and 900 °C. At 900 °C all the catalysts showed high activities, and phenol was completely converted. At 700 °C the Ni catalyst had the highest phenol conversion, and the biomass char was less active, but still more effective than the olivine. The naphthalene conversion tests were carried out at a temperature of 900 °C. The biomass char achieved nearly complete conversion of 90 g/N m^3

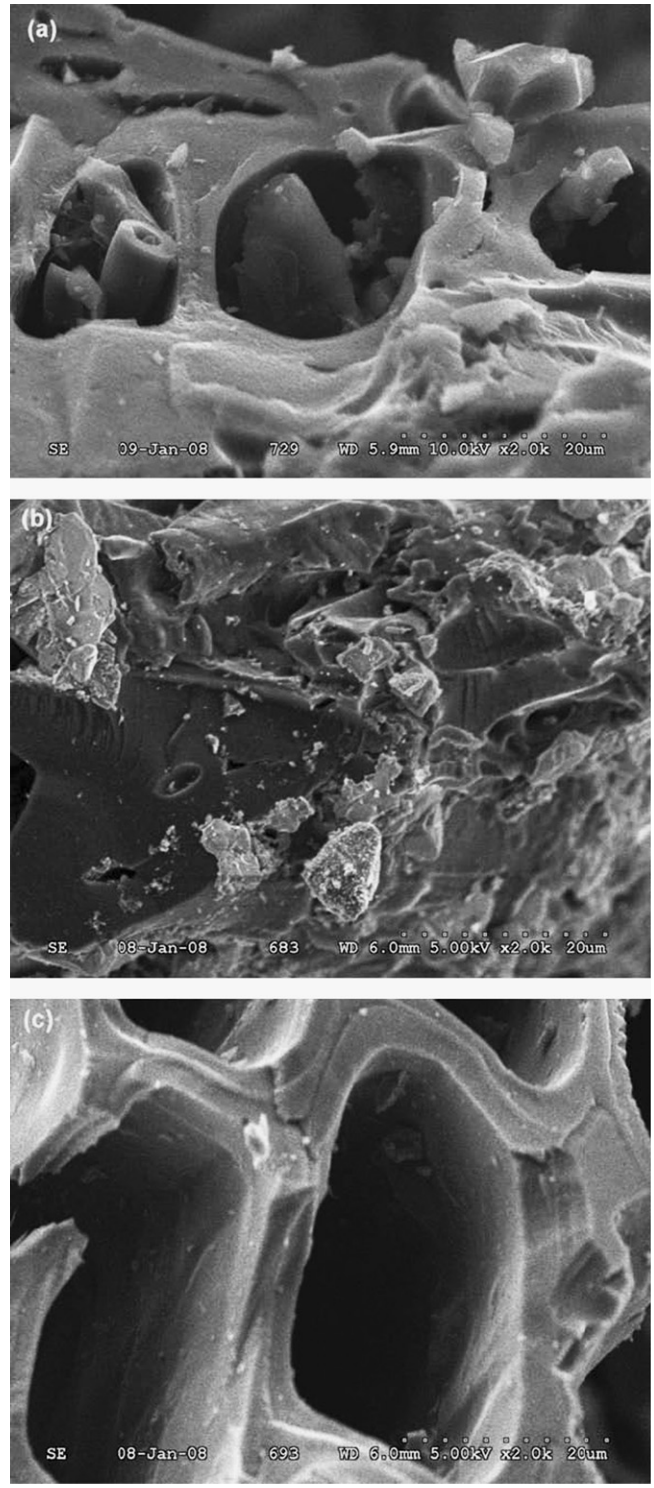


Fig. 17. SEM images for the fresh catalyst of BAC (a), Ni–Mo/BAC (b) and Ni–Mo–BAC (c) [195].

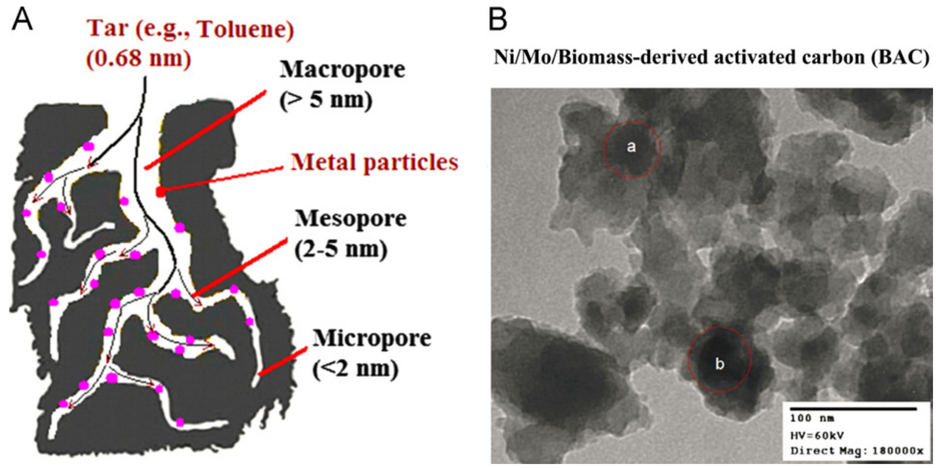


Fig. 18. (A) Roles of micropores/mesopores/micropores of a carbon-supported catalyst in tar cracking and (B) TEM micrograph of the fresh catalyst of Ni–Mo–BAC, EDX shows the atomic contents at points a and b are ~80% C, 3–4% Ni and 4–5% Mo.

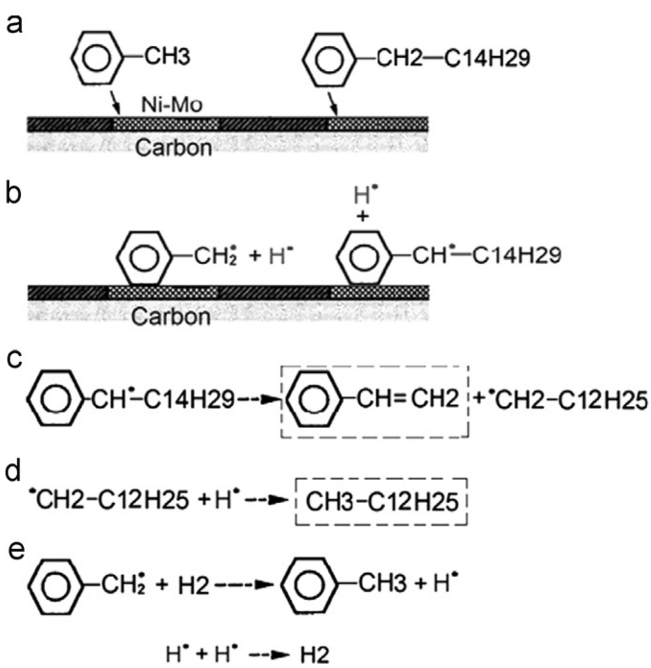


Fig. 19. Possible roles of the metal–carbon composite and supercritical toluene in hydro-conversion of asphaltene to maltene, taking *n*-pentadecylbenzene as a model compound for asphaltene [195]. (a) Adsorption of toluence and asphaltene, (b) Dissociation of toluence and asphaltene to radicals, and de-sorption of the radicals, (c) -scission of the residue-derived 2 radicals, (d) Capping of the residue-derived 1 hydrocarbon radical and (e) Regeneration of toluence and annihilation of hydrogen radical.

naphthalene, whereas the dolomite obtained only 55 wt% conversion of 40 g/N m^3 naphthalene. Being slightly inferior to the Ni catalyst, the biomass char was found to be more active for naphthalene conversions than the other catalysts tested (olivine and dolomite) [198].

AC derived from coconut shells was used in a study by Lu et al. [199] for toluene decomposition. The AC was used as a support for three copper precursors, i.e., copper nitrate, copper acetate and copper sulfate, and the effects of Cu loadings and reaction temperatures were examined. The tests were carried out using 200 ppm toluene in a N_2 gas containing 10% O_2, and at a space velocity of 40,000 h^{-1}. The copper nitrate precursor produced a catalyst with the highest toluene conversion at lower temperatures. In another study using activated carbon derived from coconut shells by Takaoka et al. [200], H_2O_2 and HNO_3 were used as an oxidizing agent to modify the AC for decomposition of pentachlorobenzene. The catalysts were prepared by mixing the AC with oxidizing agents for either 3 h or 24 h. It was observed that by oxidizing the AC, a greater number of pores were formed with larger pore diameters. In the tar decomposition tests, the temperatures varied from 300 °C to 400 °C, and GHSV maintained at 400 h^{-1} for 30 min. The HNO_3-treated AC samples (for 24 h) had high conversions of pentachlorobenzene at 98% in air and 86% in N_2 at 300 °C. At 400 °C, all catalyst samples including the untreated AC showed 100% conversion of pentachlorobenzene.

2.7. *Continuous catalytic tar reforming*

Although amounts of catalysts have been researched for tar removal and syngas composition adjustment, the activity of the catalyst can decline over time, and the catalyst can finally become poisoned if it is continuously exposed to species like sulfur, chlorine, and alkali metals, components which all are present in the raw gas to some extent [201]. It is also concluded that high tar content involves carbon formation on the catalytic surfaces, which can cause severe deactivation of the catalyst after short operating time [201,202]. Several approaches to minimize the tendency to form carbon on the surface of the catalyst are reported in the literature surveyed. For example, catalyst deactivation as a result of carbon deposits was compared in terms of fixed and fluidized beds for secondary tar cleaning by Baker et al. [203] They found that carbon deposits and catalyst deactivation was significantly lower on the catalysts in the fluidized bed. In parallel with secondary catalytic tar cleaning Seemann et al. [204] reported that the internal catalyst circulation in a fluidized bed for methanation contributed to keeping the catalyst free of carbon deposits. The methanation experiments showed that carbon deposits were formed on the catalyst in the bottom zone of the bed, and as the catalyst was transported upward in the bed, the carbon deposits were removed by hydrogenation and gasification reactions with steam. Miyazawa et al. [205] reported a lower carbon yield on various nickel catalysts during partial oxidation than during steam reforming. This phenomenon can be explained by carbon combustion with O_2 during the catalyst fluidization. Another process dealing with both the conversion of hydrocarbons and formation of carbon on active surfaces is fluid catalytic cracking [206] (FCC). In FCC reactors, the problem of carbon formation is tackled by continuous regeneration of the catalyst surfaces, in this case a zeolite.

After that, Lind [207] further proposed a novel concept of chemical looping reforming (CLR) for continuous catalytic tar reforming of biomass derived raw gas with simultaneous catalyst regeneration. Actually, the tar cleaning process explored in this work is based on the CLR process, originally presented by

Mattisson and Lyngfelt [208]. The reactor system is operated at atmospheric pressure and utilizes a circulating metal oxide (MeO) as catalyst, oxygen supplier, and heat carrier for reforming reactions and partial oxidation of the tar components into CO and H_2. The very small amount of transported oxygen by the MeO what differs this principal of CLR the most from the originally presented process. This is also the reason for why the commonly used name oxygen carrier has been changed to catalyst in this proposed tar cleaning method. The reactor system (CLR-system) consists of two reactors, one for air (AR) which is the regenerator reactor and one for the tar containing producer gas called fuel reactor (FR) or reformer reactor (Fig. 20). Two loop seals (LS), fluidized with inert gas or steam, prevent gas cross-contamination of the effluents from the respective reactor but enable the catalyst to circulate between the two reactors. In the reformer reactor, the Me_xO_y is reduced to Me_xO_{y-1} during the partial oxidation of the tar components (C_nH_m) in the raw gas according to reaction (24), which usually is an endothermic reaction [208]. Besides, the desired tar reforming reaction, additional carbon forming reactions cause carbon deposits on the Me.

$$C_nH_m + (n-n_1)Me_xO_y \rightarrow (n-n_1)CO + (0.5m)H_2 + (n-n_1)Me_xO_{y-1} + n_1C \quad (24)$$

The reduced metal oxide Me_xO_{y-1} is also acting as catalyst for tar reforming in the presence of reforming mediums* like water steam or carbon dioxide in the raw gas according to the simplified reaction (25). Simultaneously, as the Me_xO_{y-1} is reoxidized to Me_xO_y in a strongly exothermic [209,210] reaction in the AR, carbon deposits on the catalytic surfaces are oxidized to CO_2 according to reaction (25a).

$$C_nH_m + Me_xO_{y-1} + H_2O^* + CO_2^* \rightarrow C_iH_j + H_2 + CO \quad (25)$$

$$n_1Me_xO_{y-1} + n_2C + \left(\frac{n_1}{2} + n_2\right)(O_2 + 3.77N_2) \rightarrow n_1Me_xO_y + n_2CO_2 + \left(\frac{n_1}{2} + n_2\right)(3.77N_2) \quad (25a)$$

In Lind's [207] work, the method is demonstrated by using ilmenite ($FeTiO_3$) as a catalyst together with producer gas from the Chalmers biomass gasifier with a raw gas (tar content: –30 g_{tar}/N m^3). Some conclusions can be got as follows: (1) the tar cleaning concept was proven as the ilmenite was continuously transporting oxygen in the system, and the total tar content was reduced by 35%. The branched tars and phenols were to a large extent converted to pure aromatic compounds, while more activation energy was required to open the stable ring structure, i.e., benzene and naphthalene. No catalytic effects were observed from the reactor material itself or from the silica sand fillers; (2) carbon deposits on the ilmenite were continuously removed by oxidation into CO_2. Neither deactivation of the ilmenite nor disturbance in oxygen transfer was observed during the operating time; (3) the reactor system proved sufficient in order to catalytically adjust the producer gas. Ilmenite demonstrated high water gas shift reaction activity, and the H_2/CO ratio rose from approximately 0.7 in the raw gas to 3 downstream of the reactor system. A decrease in light hydrocarbons was observed, while the methane content was slightly increased downstream of the reactor system.

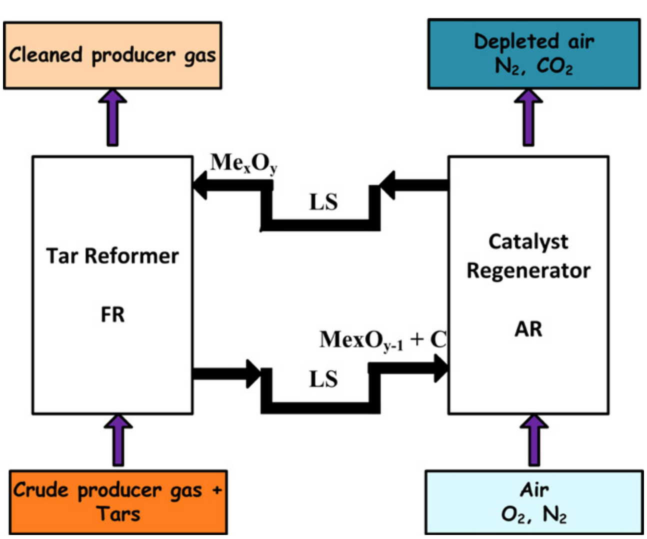


Fig. 20. Chemical looping reforming (CLR) system for tar removal [207].

3. Non-catalytic tar removal

The water scrubber is the existing technique commonly used in many gasification plants to remove contaminants and tar [211–213]. The scrubbing process, also referred to as gas absorption process, is a unit operation in which one or more contaminants of gas stream are selectively absorbed into an absorbent. Theoretically, the contaminant in the gas phase must have some solubility in the scrubbing liquid [214]. Owing to the fact that tar is a mixture of several hundreds of organics having low or no water-solubility characteristics (hydrophobic substances), water is not appropriate to be used as a scrubbing medium for tar removal. Therefore, use of other kinds of absorbents, especially hydrophobic absorbents, should be more effective for tar absorption.

In our laboratory, Phuphuakrat [215] investigated several kinds of scrubbing liquids (water, diesel fuel, biodiesel fuel, vegetable oil, and engine oil) for their absorption performances as a medium against real biomass tar without augmentation of mass transfer operation such as spray towers and packed columns. Fig. 21 presents the concentration of gravimetric tar collected at the exit of the scrubber comparing to that with no absorbent. It shows that the producer gas contained tar of 13.3 g/m^3. The concentration of the gravimetric tar decreased when scrubbed by water, vegetable oil, and engine oil, whereas it increased when scrubbed by diesel and biodiesel fuel. While using water as an absorption medium, it showed the efficiency of 31.8% for gravimetric tar removal. Water could reduce the gravimetric tar down to 9.1 g/m^3. Although most of tar components have less or no solubility in water, the decrease in the gravimetric tar by water scrubber can be attributed to condensation. The temperature of the water scrubber (28–28.5 °C) was lower than the temperature of the entering gas stream (30.8–33.6 °C). In the water scrubber, tar condensed as a separate liquid on the water surface. Because of solubility of tar, the change of

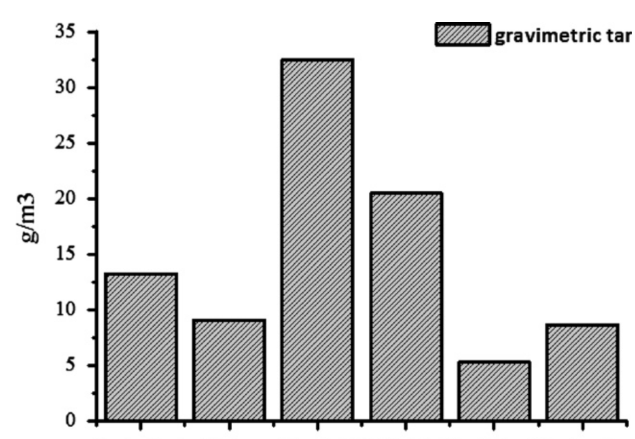


Fig. 21. Concentration of gravimetric tar at the exit of the scrubber with different absorbents.

the absorption medium from water to an oily material can be expected to improve tar removal performance. Higher tar removal efficiency was demonstrated while using vegetable and engine oils.

From Table 4, it is observed that diesel fuel shows the highest absorption efficiency for naphthalene, but it has a distinct drawback of losing the absorption medium due to easy evaporation. Although the diesel fuel vapor can be combusted in engines and does not cause fouling, it needs to refill the absorption medium in order to maintain the gas residence time in the scrubber. Moreover, diesel fuel is not economical. Therefore, vegetable oil can be selected to absorb biomass tar. Even though vegetable oil also shows a high absorption performance for light aromatic hydrocarbon tars (especially benzene, toluene, and xylene) reducing the heating value of the producer gas, the absorbed light aromatic hydrocarbon tars (especially benzene, toluene, and xylene) can be recovered by desorption (stripping) [216].

Table 4
Absorption efficiencies of tar components by different absorbents (%).

	Water	Diesel fuel	Biodiesel fuel	Vegetable oil	Engine oil
Benzene	24.1	77.0	86.1	77.6	61.7
Toluene	22.5	63.2	94.7	91.1	82.3
Xylene	22.1	−730.1	97.8	96.4	90.7
Styrene	23.5	57.7	98.1	97.1	91.1
Phenol	92.8	−111.1	99.9	99.7	97.7
Indene	28.2	97.9	97.2	97.6	88.7
Naphthalene	38.9	97.4	90.3	93.5	76.2

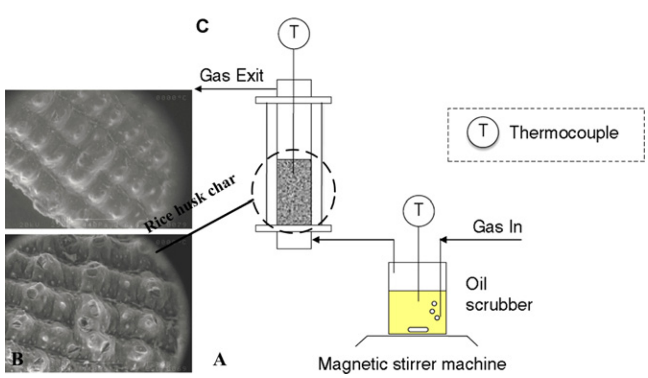


Fig. 22. Schematics of each type of gas cleaning unit (A): combination of the oil scrubber and the adsorbent bed for the combination of absorption and adsorption and (B) Scanning electron microscope (SEM) micrograph of rice husk and rice husk char.

Then, Paethanom [217] continued to investigate heavy tar removal by absorption using vegetable oil and waste-cooking oil scrubbers and light tar removal by adsorption using rice husk and rice husk char adsorbent bed shown in Fig. 22(A). It can be seen that after high temperature gasified, rice husk char became a highly porous material. Therefore, this char was found to have suitable characteristics to be used as a tar removal adsorbent (Fig. 22(B)). It was indicated that, in all conditions, vegetable oil showed better tar removal performance and the optimum mixing speed was 1000 rpm for the vegetable oil scrubber and 750 rpm for the waste cooking oil (Fig. 23(A)). This can be explained that, contaminants in waste cooking oil, such as nitrogen and sulfur [217], weaken the Van der Waal's force between oil molecules and absorbed tar. Therefore, with a too high mixing speed, not only contaminants but also absorbed tar would de-absorb and flew out with the flowing out gas. And the experiment of combination of the vegetable oil scrubber with no mixing and 1000 rpm mixing speed combined rice husk char adsorption was set up and achieved 89.8% and 95.4% gravimetric tar removal efficiency, respectively, as shown in Fig. 23(B). The tar removal efficiency was almost the same in the cases of vegetable oil scrubbing without stirring combined with adsorption and vegetable oil scrubbing with 1000 rpm mixing speed. These results show an interesting fact that the combination system showed the highest tar removal efficiency with the economically feasibility using low-cost char produced in the gasification process as an effective carbon adsorbent, which was a bonus advantage from gasification system itself [218].

For absorption, vegetable oil and waste-cooking oil were found to be effective absorbent for gravimetric tar removal. It was found

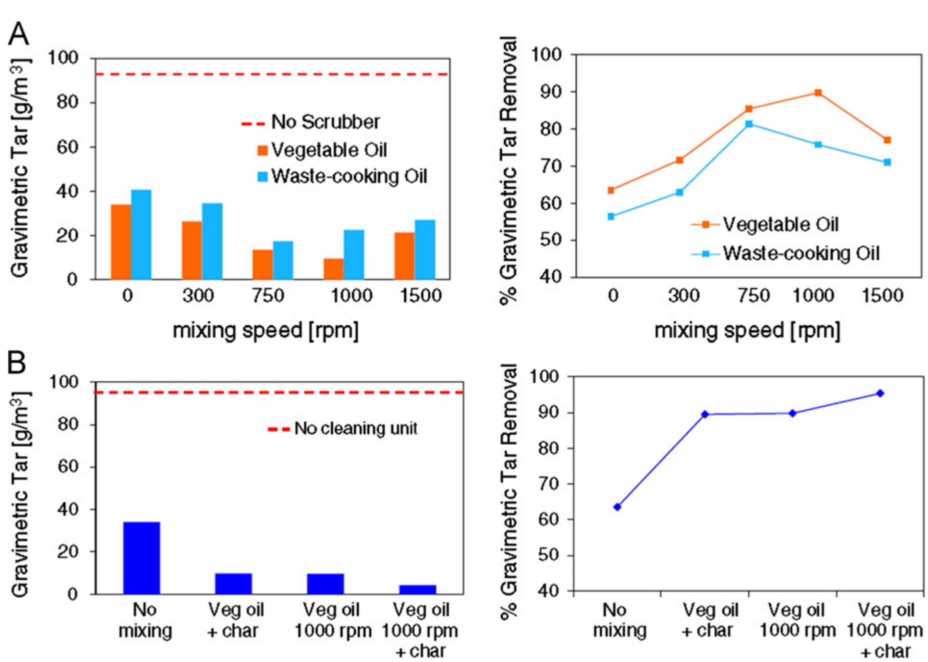


Fig. 23. (A) Turbulent mixing effect of the vegetable oil and waste-cooking oil scrubbers on tar removal and (B) Tar removal performance of the combination of vegetable oil scrubber with rice husk char adsorption bed at each case. [218].

that the combination of these two techniques created positive synergetic effect that heavy tar, which is mostly oily liquid or solid at ambient temperature, will be firstly absorbed and removed by vegetable oil scrubber then the remain light tar in the producer gas, which is mostly in gas phase, will be adsorbed and removed by rice husk char and release gratified tar-free producer gas to the downstream application.

4. Conclusions

Biomass conversion into producer gas in the gasification process is very useful because it can be used as an alternative fuel to replace the fossil fuels for heat and power generation. The successful application of producer gas depends not only on the quantity of tar, but also on the properties and compositions of tar, which is associated with a dew-point of tar components. It is worthy for researchers to seek variety of reasonable catalysts for tar reforming and removal. In our point, an excellent catalyst should have some advantages, just like high efficiency of tar elimination, environmental friendly (no secondary pollution), low cost and easy regenerability. Thus, further research work on catalytic tar elimination during biomass gasification needs to be done in the following areas: (1) Energetically develop the nano-catalysts because of high tar reforming efficiency and excellent catalysis property, i.e., nanoarchitectured $Ni_5TiO_7/TiO_2/Ti$ compound composite as a catalyst in a biomass gasification process have proven outstandingly active as catalysts and appear most suitable for high-temperature operation in biomass gasification featuring high efficiency and long-term stability. (2) Select reasonable catalysts according to the tar types, tar concentration. If higher concentration of naphthalene, Ni/ZY-80 and Ni/ZY-30 can be utilized for tar reforming; (3) Set up the recycling systems for tars elimination and catalysts regeneration, i.e., chemical looping reforming (CLR) for continuous catalytic tar reforming of biomass derived raw gas with simultaneous catalyst regeneration; (4) Combination of catalytic tar elimination under higher temperature and tar adsorption with absorbents under ambient temperature. Significantly, the remained tar in the syngas can be effectively scrubbed by waste oil materials replace of water after catalytic tar reforming in the gasifiers.

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